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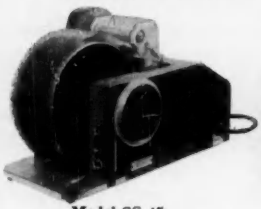

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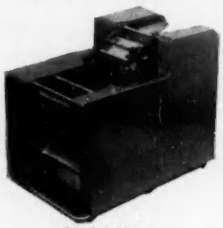

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TEXTILE RESEARCH JOURNAL

The Migration of Liquids in Textile Assemblies

Part II: The Wicking of Liquids in Yarns

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Introduction

It has previously been shown that when a liquid wicks in a textile yarn or yarn system such as a woven fabric under circumstances where the effect of gravity is negligible, the rate at which the liquid front advances is described by an equation of the form

$$s = kt^{\frac{1}{2}} \tag{1}$$

where s is the distance traveled, t is the time, and k is a constant characteristic of the yarn–liquid system [1]. The factors which determine k can be separated by considering the well-known Washburn equation for the rate of flow in a cylindrical capillary tube, from which Equation 1 is deduced.

Washburn's equation for capillary migration in the absence of gravitational effects (for example, migration in a horizontal capillary tube) may be written in the following form:

$$\frac{ds}{dt} = \frac{2\gamma r \cos\theta}{8\eta s} \tag{2}$$

where γ is the surface tension of the liquid, r is the radius of the capillary tube, θ is the contact angle between the liquid and the substance composing the wall of the tube, and η is the viscosity of the liquid.

It is evident that Equation 1 can be derived from Equation 2 provided that we equate k^2 to a numerical factor times the quantity

$$\frac{\gamma r \cos\theta}{\eta} \tag{3}$$

Since a yarn is not geometrically equivalent to a capillary tube we must substitute for r a suitably derived "equivalent radius" of the open cross-sectional area within the yarn. A numerical value for r in any given yarn is difficult to determine. It may be assumed as a first approximation, for yarns composed of oriented cylindrical fibers, that r will be proportional to the square root of the open cross-sectional area. This assumption is compatible with the concept of the hydraulic depth widely used in considering flow through porous media [3]. The only other factor in Expression 3 which might be ambiguous is the contact angle θ. In systems where there is hysteresis of the contact angle, the advancing contact angle is considered to control capillary motion of the liquid forward over fresh unwetted solid surface.

It is also noteworthy that Equation 2 applies only to systems where the free surface of the liquid reservoir feeding the capillary tube is substantially flat; i.e., the capillary pressure on the reservoir surface is zero. In systems where the reservoir itself is of

capillary dimensions, Equation 2 is not applicable; such systems are considered in one of the sections of this paper.

The purpose of these investigations was to study experimentally the wicking behavior of a series of inert, nonvolatile organic liquids in typical yarns, paying particular attention to the effects of viscosity and surface tension of the liquid, contact angle relationships, and geometry of both the yarn and the yarn–liquid system.

Materials

The yarns and their preparation are described below in the sections covering the individual experiments.

The liquids which were used were selected for their low volatility, high stability, and low or well-determined hygroscopicity. They were also selected to represent limited ranges of viscosity, surface tension, contact angle, and contact angle hysteresis. The methods by which the contact angle and contact angle hysteresis were measured are described in another paper [2]. Viscosity, surface tension, and density were determined by standard procedures. In order to facilitate observation of the liquid front within the yarn, the liquids were colored with 0.2% of either Oil Soluble Red (Du Pont) or the acid dye Fast Red A. It was established in separate experiments that these dyes had negligible effects on the wicking and on the measured properties of the liquid.

Effect of Yarn Tightness and Fiber Cross Section on Wicking

In this work single yarns having accurately known and controlled construction and relatively simple geometry were used, since this type of system makes it possible to separate the effects due to liquid properties from the effects due to fabric geometry. Nylon and viscose rayon filament yarns were used.

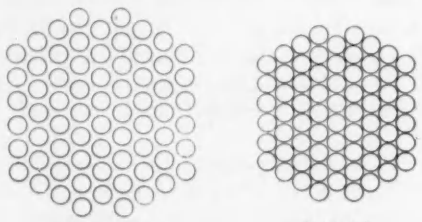

Fig. 1. Diagrammatic cross sections to scale of 68-filament nylon yarns.

In the studies with nylon, the test yarns were prepared from 68-filament 140-den. yarns. The individual filaments were essentially cylindrical. The yarns were cleaned by washing in Dreft solution followed by extraction with hot ethanol. They were then untwisted and retwisted under tension to the desired turns per centimeter. After being twisted, the yarns were clamped in a frame which maintained the twist and tension, permitted one end to be dipped into the test liquid, and possessed a scale for measuring the height of liquid travel. The frame was supported vertically so that the bottom of the yarn was submerged to a depth of at least 1 cm. in the liquid. The liquid was contained in a vessel wide enough to accommodate the frame with at least 1 cm. clearance on all sides between the frame and the vessel walls. The height of the liquid in the yarn was observed at various time intervals up to 24 hr. or until the liquid height was 12 cm. The experiments were conducted in a room with a controlled relative humidity of 68% and a temperature of 70° F.

Two sets of experiments were conducted using yarns of different twist and tension which will be referred to as loose yarn and tight yarn. The loose yarn had 4.4 turns/cm. and 20 g. tension; tight yarn had 10 turns/cm. and 177 g. tension. From the yarn diameters, the number of filaments, and the filament diameter (16 μ), the total cross-sectional area of the empty space between the filaments in the yarn was calculated to be 6600 μ^2 for the loose yarn and 1650 μ^2 for the tight yarn. Thus the channel cross section in the loose yarn was four times that in the tight yarn, and the equivalent capillary radius in the loose yarn was, to a first approximate, twice the equivalent capillary radius in the tight yarn. Diagrammatic cross sections of the loose and tight yarns are shown in Figure 1; the physical properties of the liquids used are given in Table I.

The wicking behavior of each of the following liquids was observed in the loose nylon yarn and the results were plotted as height of rise vs. square root of time.

Liquid	Abbreviation
Dibutyl butyl phosphonate	DBBP
Ucon LB-65	U-65
Ucon 50-HB-55	U-55
Diethylene glycol	DEG
2-Anilinoethanol	AE
Polyethylene glycol 400	PEG
Oleic acid	OA

These plots, shown in Figure 2, are straight lines, since the runs were stopped before the liquids

reached a height at which gravity would have any significant influence on the rate. The equilibrium wicking height of a typical test liquid in this yarn would be on the order of 2 m.

The data obtained with the tight yarn was plotted in a similar manner and compared with the data from the loose yarn. The two curves for oleic acid are shown in Figure 3.

In the two yarns under study, the ratio of the wicking rates (expressed as cm.²/min.) should be equal to the ratio of the equivalent capillary radii, which had been estimated to be 2. The ratio of

TABLE I. Properties and Wicking Rates of Liquid–Yarn Systems

Abbreviation	Liquid	Fabric or yarn	*K* value†	Slope of rate curve, cm./min.½	Viscosity of liquid, 25° C., centistokes	Surface tension, 20° C., dynes/cm.	Maximum measured advancing contact angle (Wilhelmy Pull)‡, degrees	Minimum measured receding contact angle (Wilhelmy Pull)‡, degrees	Maximum advancing contact angle (Photo)‡, degrees	Minimum receding contact angle (Photo)‡, degrees	Density (20° C.), g./ml.
DBBP	Dibutyl butyl phosphonate	Loose nylon yarn	20.4	1.26	1.5	30.6	—	—	—	—	.948
U-65	Ucon LB-65		1.94	.66	17	33	—	—	0	0	.96
U-55	Ucon 50-HB-55		2.58	.56	13	34.8	15 (.966)	0	0	0	.99
DEG	Diethylene glycol		1.22	.525	30	48	—	—	40 (.766)	15 (.966)	1.12
OA	Oleic acid		1.03	.44	30.9	32.5	0	0	0	0	.89
AE	2-Anilinoethanol		.92	.23	49	45	—	—	0	0	1.11
PEG 400	Polyethylene glycol 400		.41	.12	87	49	37 (.799)	22 (.927)	43 (.731)	6 (.994)	1.13
	Dibutyl butyl phosphonate	Tight nylon yarn	20.4	.69	1.5	30.6	—	—	—	—	.948
	Ucon LB-65		1.94	.35	17	33	—	—	0	0	.96
	Ucon 50-HB-55		2.58	.35	13	34.8	15 (.966)	0	0	0	.99
	Oleic acid		1.03	.32	30.9	32.5	0	0	0	0	.89
	2-Anilinoethanol		.92	.18	49	45	—	—	0	0	1.11
	Polyethylene glycol 400		.41	.070	87	49	37 (.799)	22 (.927)	43 (.731)	6 (.994)	1.13
DES	Diethyl sebacate	Loose viscose yarn	6.2	2.2	5.3	32.9	—	—	0	0	.965
	Ucon LB-65		1.94	1.00	17	33	—	—	0	0	.96
	Oleic acid		1.05	.90	30.9	32.5	—	—	0	0	.89
	2-Anilinoethanol		.92	.73	49	45	—	—	0	0	1.11
	Diethyl sebacate	Tight viscose yarn	6.2	1.0	5.3	32.9	—	—	0	0	.965
	Ucon LB-65		1.94	.32	17	33	—	—	0	0	.96
	Oleic acid		1.05	.40	30.9	32.5	—	—	0	0	.89
	2-Anilinoethanol		.92	.29	49	45	—	—	0	0	1.11
DEG		Cotton yarn (filling, 8¼ sateen, 20 g. tension)	1.21	2.3	30	48	—	—	41 (.755)	25 (.906)	1.12
	Ucon 50-HB-55		2.68	1.87	13	34.8	—	—	0	0	.99
	Oleic acid		1.05	1.53	30.9	32.5	—	—	0	0	.89
PEG 400			.24	.75	87	49	—	—	65 (.422)	9 (.988)	1.13
	Oleic acid	Wool yarn (Lebanon flannel filling, 20 g. tension)	1.04	.96	30.9	32.5	8.5 (.989)	0	0	0	.89
DEG			.80	.33	30	48	42.7 (.735)	0	60 (.500)	6 (.994)	1.12
PEG 400			.21	.29	87	49	54.9 (.573)	26.7 (.893)	68 (.374)	18 (.951)	1.13
	Ucon 50-HB-55	Stacks of cotton sateen	2.68	.77	13	34.8	—	—	0	0	.99
PEG 400			.24	.25	87	49	—	—	65 (.422)	9 (.988)	1.13
	Tetralin	Cotton shirting warp (80 × 80)	14.2	4.3	2.34	33.3	—	—	—	—	.971
	Decalin		10.5	3.9	3.04	32.1	0*	0*	—	—	.896
	Lactonitrile		16.1	3.6	2.26	36.7	0	0	—	—	.992
	n-Butanol		5.75	3.5	4.27	24.6	0*	0*	—	—	.8098
	i-Butanol		4.82	2.8	4.76	23.0	0*	0*	—	—	.8011
	Tetralin	Wool flannel Lebanon 425, warp	14.2	6.4	2.34	33.3	—	—	—	—	.971
	Decalin		10.5	5.7	3.04	32.1	0	0	—	—	.896
	n-Butanol		5.75	5.6	4.27	24.6	0	0	—	—	.8098
	i-Butanol		4.82	5.6	4.76	23.0	0	0	—	—	.8011
	Cyclohexanone		10.6	4.7	3.12	34.4	15 (.966)	0	—	—	.9478
	Lactonitrile		13.3	1.33	2.26	36.7	35 (.819)	22 (.927)	—	—	.992

* Wilhelmy pulls measured on viscose bristle.
† *K* value = surface tension × cos of maximum contact angle × (1/viscosity).
‡ Figure in parenthesis = cosine.

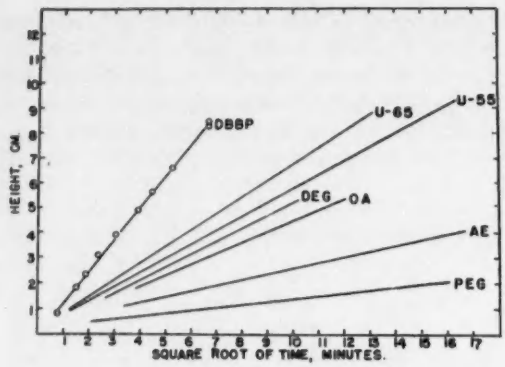

Fig. 2. Rise of various liquids in loose nylon filament yarn. Dibutyl butyl phosphonate (DBBP); Ucon LB-65 (U-65); Ucon 50-HB-55 (U-55); diethylene glycol (DEG); oleic acid (OA); 2-anilino-ethanol (AE); and polyethylene glycol 400 (PEG).

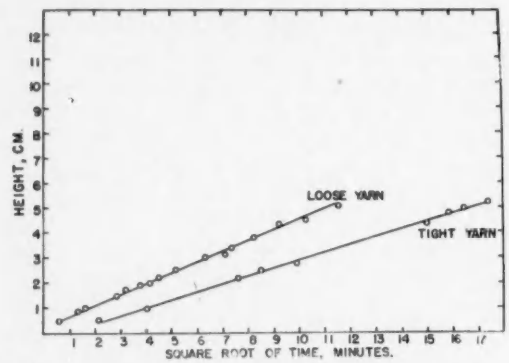

Fig. 3. Rise of oleic acid at 70° F. and 65% relative humidity in loose and tight 68-filament nylon yarns.

wicking rates, loose yarn to tight yarn, for oleic acid was calculated and found to be 1.9, considered in excellent agreement with the theoretical value of 2. The calculated ratios of wicking rates for other test liquids in the two nylon yarns are given in Table II. These ratios are reasonably close to the theoretical value of 2, with the exception of diethylene glycol, which deviates markedly.

Although the reason for this anomalous value in the diethylene glycol system was not established, there are at least two hypothetical reasons which might be considered. First, diethylene glycol is the most hygroscopic of the liquids used in these studies, and the pick-up of atmospheric moisture during the wicking experiments may have had an effect on its wicking rate. Under the conditions of the experiments, 65% relative humidity, diethylene glycol can take up 15–20% of moisture in 24 hr. The only other hygroscopic liquids were the two Ucons and polyethylene glycol 400 which take up about 3, 3, and 6% moisture respectively under the same conditions. It is probable that the advancing contact angle of the diethylene glycol increases as the moisture content increases, and the more rapid uptake of atmospheric moisture in the smaller capillaries could account for the abnormally low wicking rate. Second, combination of diethylene glycol with a small amount of water might swell the fibers and tend to close the channels in the yarns. This effect would be proportionately greater in the tight yarn than in the loose yarn.

TABLE II. Ratio of Equivalent Capillary Radius in Loose Yarn to Equivalent Capillary Radius in Tight Yarn, Calculated from Rates of Rise of Various Liquids

Liquid	Nylon*	Viscose*
Dibutyl butyl phosphonate	3.3	—
Diethyl sebacate	1.8	4.8
Ucon LB-65	3.5	9.8
Ucon 50-HB-55	2.6	—
Diethylene glycol	18.9	30+
Oleic acid	1.9	5.0
2-Anilino-ethanol	1.6	6.3
Polyethylene glycol 400	2.8	—

* Yarn descriptions in text.

The rise of several of the liquids listed in Table I was also observed in viscose filament yarns of known geometry using the same techniques used with nylon yarns. The "loose" viscose yarn was prepared from 35-filament 200-den. bright viscose by imparting a twist of 2 turns/cm. and a tension of 20 g. Assuming the filaments to have a uniform circular cross section, the total open cross-sectional area was calculated to be 13,900 μ^2. This calculation was based on microscope measurements of yarn diameter and filament diameter. The "tight" viscose yarn was prepared by imparting a twist of 10 turns/cm. and 20 g. tension. The calculated open cross-sectional area for the tight yarn was 8,200 μ^2. Thus, the theoretical ratio of the equivalent capillary radii of the two yarns (r_{loose}/r_{tight}), calculated as in the case of the nylon yarns, was 1.3.

The data were plotted as height of rise vs. square root of time. Four of the liquids examined gave linear plots in both the loose yarn and the tight yarn. These were diethyl sebacate, 2-anilinoethanol, oleic acid, and Ucon LB-65. Diethylene glycol behaved abnormally, as it did in the nylon yarns. With

diethylene glycol the wicking essentially stopped in the tight viscose yarn after 15–30 min., and it was also noticed that the loose yarn tended to go slack during the wicking. This was probably due to swelling from the atmospheric moisture pick-up by the diethylene glycol during the experiment. From the plots of the data the ratios of the equivalent capillary radii (r_{loose}/r_{tight}) were calculated and are shown in Table II. These ratios were all much higher than the 1.3 calculated from the yarn geometry. Again the greatest deviation from the calculated value was observed with diethylene glycol. With this liquid the ratio increased as wicking progressed, going from 3 to over 30.

A comparison can be made between the wicking rates in nylon yarn and the wicking rates in viscose yarn on the basis of the open cross-sectional areas in the two yarns. In the loose yarns the ratio of equivalent capillary radii $r_{viscose}/r_{nylon}$ should be equal to the square root of 13900/6600, or 1.45. In the tight yarns the ratio of equivalent capillary radii should, by a similar calculation, be 2.23. These ratios should also be equal to the ratios of the corresponding $s(ds/dt)$ values, i.e., to the slopes of the rate curves expressed as cm.^{2}/min.

The data in Table I for two test liquids, oleic acid and 2-anilinoethanol, show good agreement in the tight yarns between the observed rate ratio and the theoretical rate ratio of 2.23 calculated above. In the loose yarns, however, the agreement was poor, with the wicking rate in viscose yarn being abnormally high.

This effect, as well as the anomalous high r_{loose}/r_{tight} value observed for the two viscose yarns, can possibly be attributed to the crenulated cross section of the viscose fiber. Figure 4 represents a cross section of three adjacent filaments in a nylon yarn and a viscose yarn. It is evident from the crenulated cross section of the viscose filament that the open cross-sectional area in a loose yarn, calculated from the microscopically observed diameter, will be greater than the real cross-sectional area. This would account, at least in part, for the migration in this yarn being faster than predicted by the theoretical calculations. When the viscose yarn is tightened by tension and twisting, the irregular cross section affords the possibility of very tight packing. If the crenulations mesh like gear teeth, the open space can be reduced greatly without any corresponding reduction in the yarn diameter. Thus the wicking rate in the tight viscose yarns could readily be diminished to the level observed.

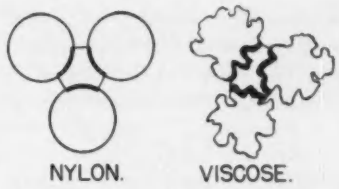

Fig. 4. Schematic packing of nylon and viscose filaments.

Effect of Physical Properties of the Liquid on Wicking

If a yarn can indeed be regarded as the equivalent of a capillary tube, the wicking rate, according to Equation 2, should vary directly as the surface tension of the wicking liquid and the cosine of the contact angle and inversely as the viscosity. These three factors, expressed in suitable units, may be combined into a single factor which we have for convenience called K. In any single yarn system the equivalent radius r is constant regardless of what wicking liquid is used, provided the liquid does not react with the yarn to alter its geometry. Thus, for a series of liquids in a given yarn the wicking rates should fall in the same order as the K values, a high wicking rate corresponding to a high K value. Table I shows the slopes of the rate curves of the various liquid–yarn wicking systems which were examined, together with the K values and the individual physical properties which have an effect on the wicking rate.

In all of the yarn and fabric systems there is reasonably good qualitative correlation between the K value and the wicking rate. In the viscose yarns, the wool yarn, and the stacks of cotton sateen swatches, there are no liquids which show anomalous behavior. In the cotton yarn, diethylene glycol showed a higher wicking rate than its K value would indicate. This may be due to the hygroscopicity of this compound. It is possible that uptake of atmospheric moisture during the measurements might have occurred. This would tend to increase the surface tension while decreasing the viscosity and the advancing contact angle. These changes would all tend to increase the wicking rate to a value greater than predicted. In both the cotton and wool fabrics, lactonitrile showed an abnormally slow wicking rate. It is possible that this may be due to a swelling effect of lactonitrile on the cellulosic and keratin fibers, thus causing the channels of flow to shrink and r to be-

come correspondingly smaller. A similar swelling effect may be responsible for the abnormally low wicking rate of cyclohexanone in wool fabric. No positive evidence for swelling in these systems, however, has as yet been gathered. The anomalous reversal with regard to wicking rates of Ucon LB 65 and Ucon 50HB55 in the nylon yarns is unexplained.

The Wicking of Droplets and Limited Quantities of Liquid

It has been shown in a previous paper of this series [1] that wet spots formed on a single test swatch of woven fabric by uniformly sized droplets or small splashes of liquid do not necessarily spread to the same ultimate area. Different liquids, depending on their physical characteristics, spread to differing extents before the spreading (which is really a wicking in the yarns and a transfer of liquid from yarn to yarn at the cross-over points) eventually stops.

A single yarn is a much simpler system than a fabric in which to study this phenomenon and determine the factors which control it.

When a yarn is mounted horizontally, all effects of gravity on the wicking rate become negligible. Under these conditions Equation 2 remains valid as long as more liquid is always available to the yarn than the yarn can take up and the surface curvature of the liquid in the supply system is very small as compared with the curvature at the advancing front within the yarn.

A single droplet of liquid placed on a yarn forms a reservoir of limited capacity. As wicking proceeds and this reservoir becomes progressively depleted, it is evident that Equation 2 must at some point cease to express accurately the rate of wicking. In order to study the wicking process under conditions of limited liquid supply, the behavior of single droplets of liquid on horizontal yarns was studied as follows.

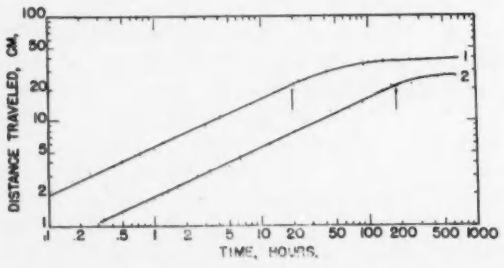

Fig. 5. Advance of liquid front in loose nylon yarn. Arrows indicate time at which drop disappeared. Curve 1: Ucon 50-HB-55 (2.0-mg. drop). Curve 2: Polyethylene glycol 400 (1.6-mg. drop).

The yarns were cleaned before use by washing in warm Dreft or other light duty household detergent solution, followed by extraction in boiling 95% ethanol. They were then mounted in a frame designed to hold the yarn in a horizontal position, to impart and maintain any desired degree of twist, and to maintain a constant controllable tension on the yarn during wicking. The frame was mounted sufficiently close to a scale so that the position of the liquid front could easily be read on either side of the zero mark with a precision of about 1 mm.

A droplet of the colored liquid to be tested was placed on the yarn opposite the zero mark. This droplet was conveniently dispensed from a micrometer hypodermic syringe so that the weight was known with reasonable precision. The droplet was made large enough so that it did not soak into the yarn immediately, nor even within a few minutes. For most of the yarn–liquid systems studied, droplets weighing in the range of 3–10 mg. were found to be satisfactory.

The position of the liquid fronts (on each side of the zero point) was observed and plotted on log paper as a function of time. In all cases the time at which the liquid droplet finally disappeared within the yarn was carefully noted. Figure 5 shows the wicking rate plots for Ucon 50HB55 and PEG 400 in the loose nylon yarn. The time at which the droplets ceased to be visible on the yarn exterior is indicated on the curves. It is evident that in this time region the curves started to become nonlinear and the wicking decelerated progressively. After a period of continuous deceleration the liquid reached a substantially static condition. We shall refer to the liquid migration after the drop disappears (sinks completely into the yarn) as "wicking from a limited reservoir." During the period before the drop disappears the wicking rate curve is linear and is similar to the wicking rate curves obtained from a flat or unlimited reservoir.

It is evident from the curves in Figure 5 that after reaching the limited reservoir state the Ucon 50 HB55 continued to wick further and for a longer time than the PEG 400 before they both ultimately stopped. A similar effect with the same two liquids was obtained when cotton yarns were used as the wicking media. On woolen yarns the two liquids showed an even more marked dissimilarity in their wicking behavior throughout the limited reservoir

range. This dissimilarity was noted not only with the two liquids mentioned above. All the liquids tested (on any one yarn system) appeared to differ at least slightly from one another in their ability to continue wicking in the limited reservoir range. In general, however, the liquids fell into two groups: those which wicked extensively (similar to Ucon 50HB55 in the above examples) and those which stopped relatively shortly after entering the limited reservoir range (similar to PEG 400).

This diverse behavior is attributed to the difference in contact angle hysteresis among the various fiber–liquid systems. It is evident that in the limited reservoir system described above any wicking which occurs must correspond to a movement of liquid from one set of capillary spaces within the yarn to another. In systems having a contact angle less than 90° this movement must proceed from larger spaces into smaller ones, i.e., into spaces having greater liquid–solid interface area per unit liquid volume. The part which contact angle hysteresis can play in this type of wicking is best understood by considering the well-known equation for capillary pressure p in cylindrical capillaries:

$$p = \frac{2\gamma \cos \theta}{r}$$

γ = surface tension, θ = contact angle, and r = radius of capillary. Where a large capillary R is connected to a small one A, the net pressure acting to move liquid out of the large capillary into the small one is

$$\Delta p = p_A - p_R = \left(\frac{2\gamma \cos \theta_A}{r_A}\right) - \left(\frac{2\gamma \cos \theta_R}{r_R}\right)$$

Where there is no contact angle hysteresis, $\theta_A = \theta_R$, and the liquid will all move into the small tube A. This is because r_A is smaller than r_R, and Δp is therefore positive.

Now consider what happens if there is contact angle hysteresis. As the liquid moves into tube A, θ_A becomes an advancing contact angle, greater than the equilibrium angle. θ_R becomes a receding contact angle, less than the equilibrium angle and much less than θ_A. Δp becomes zero and the liquid stops moving when the following relationship holds:

$$\frac{\cos \theta_A}{\cos \theta_R} = \frac{r_A}{r_R}$$

The wicking of a limited volume (e.g., a single drop) of liquid in a fabric after initial entry into the fabric consists essentially of movement from large capillary spaces into small capillary spaces. Since high contact angle hysteresis inhibits this movement, as shown above, it also inhibits wicking.

Since the ultimate distance traveled by a given weight of liquid in a limited reservoir yarn system varies from liquid to liquid, it is evident that the average quantity of liquid per unit length of yarn must also vary. The quantity of liquid held by a unit length of yarn may be referred to as the "line density" of the liquid. The line density within a uniform cylindrical tubular capillary is, of course, always constant and is equal to the weight of the liquid filling a unit length of the tube. In a yarn, however, the line density may be far below the theoretical maximum which corresponds to having all open spaces filled with liquid. Even in an unlimited reservoir system the line density near the advancing front is well under the theoretical maximum. Thus the liquid is advancing in certain preferred grooves and interfiber spaces while other parallel spaces equidistant from the reservoir are empty.[1]

Table III shows the average line density (over the whole length of yarn from the site of the original reservoir droplet to the farthest point of advance) for four typical wicking liquids in a woolen yarn system. The two liquids of high contact angle hysteresis show a much higher line density than the liquids of low contact angle hysteresis. In the high line density

[1] This problem has been analyzed mathematically by Palmer [3]. After making a few simplifying assumptions about the yarn geometry, etc., an expression is derived for the line density at any point along a vertical wicking yarn during the unlimited reservoir stage.

TABLE III. Wicking of Single Droplets in Wool Yarn

Yarn: Filling from flannel Lebanon 425

Liquid	Ucon 50-HB-55	Oleic acid	Diethylene glycol	Polyethylene glycol 400
Drop size, mg.	3.7	3.7	4.5	5.6
Length of wetted yarn after wicking had stopped, cm.	20	31	14	19
Avg. line density, mg. of liquid/cm. of yarn	.18	.12	.31	.29

systems the liquid has failed to move from the channels of *fastest* migration, where it originally collected, into the channels of *farthest* migration which must, by simple geometry, be narrower.

A better insight into this aspect of wicking was obtained by determining the line density from point to point along the test yarns at various stages of the wicking process. A typical system consisted of the loose nylon yarn referred to above and Ucon 50 HB55 containing 1% Du Pont Oil Soluble Red Dye. To measure the distribution of liquid in the yarn as a function of time, a small drop of liquid (about 2.5 mg.) was placed on a horizontally held length of yarn, and was allowed to wick for a predetermined period of time. The position of the two liquid fronts was noted, and the yarn was then cut into a suitable number of lengths, depending on how far the liquid had wicked. Each section was then extracted with carbon tetrachloride and the quantity of Ucon present was determined colorimetrically. The average quantity of liquid present per centimeter length of yarn in each of the analyzed sections was calculated. Several replicate runs were made. The distributions observed in separate runs were surprisingly replicable, and the data given below represent selected individual runs rather than averages. Figure 6 shows the plots of line density vs. distance from the origin for a series of drops of approximately the same size (1.05–1.08 mg.) which required about 18 hr. to completely sink into the yarn. During the infinite reservoir stage (Figures 6 A–D), the total liquid present in the yarn increases and the region where the liquid has the maximum line density of about 0.06 mg./cm. continues to expand outward until it reaches about 15 cm. from the origin. Figure 6D represents the distribution just after the drop has disappeared into the yarn at the origin. Figures 6D–G show the change in liquid distribution along the yarn during the whole period of limited reservoir wicking. In this low-hysteresis Ucon 50HB55–nylon system, the liquid front advanced from about 21 to about 39 cm. The line density near the origin progressively decreased. In the final configuration, when wicking had substantially stopped (Figure 6G), the distribution curve sloped steadily without any noticeable long plateaus from the origin to the liquid front.

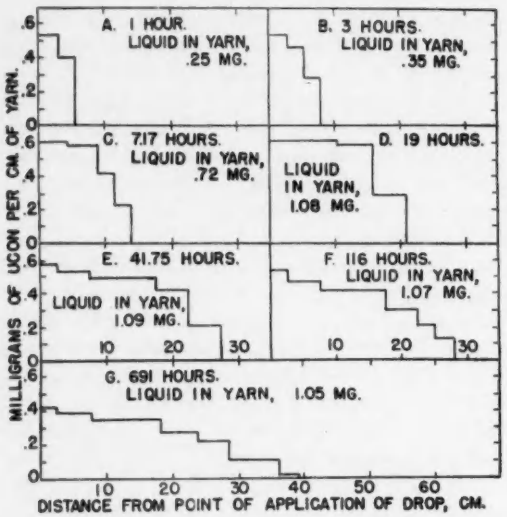
A. 1 HOUR. LIQUID IN YARN, .25 MG.
B. 3 HOURS. LIQUID IN YARN, .35 MG.
C. 7.17 HOURS. LIQUID IN YARN, .72 MG.
D. 19 HOURS. LIQUID IN YARN, 1.08 MG.
E. 41.75 HOURS. LIQUID IN YARN, 1.09 MG.
F. 116 HOURS. LIQUID IN YARN, 1.07 MG.
G. 691 HOURS. LIQUID IN YARN, 1.05 MG.
MILLIGRAMS OF UCON PER CM. OF YARN.
DISTANCE FROM POINT OF APPLICATION OF DROP, CM.

Fig. 6. Distribution of Ucon 50-HB-55 in loose nylon yarn.

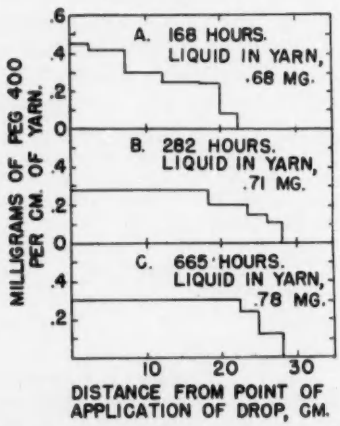
A. 168 HOURS. LIQUID IN YARN, .68 MG.
B. 282 HOURS. LIQUID IN YARN, .71 MG.
C. 665 HOURS. LIQUID IN YARN, .78 MG.
MILLIGRAMS OF PEG 400 PER CM. OF YARN.
DISTANCE FROM POINT OF APPLICATION OF DROP, CM.

Fig. 7. Distribution of polyethylene glycol 400 in loose nylon yarn.

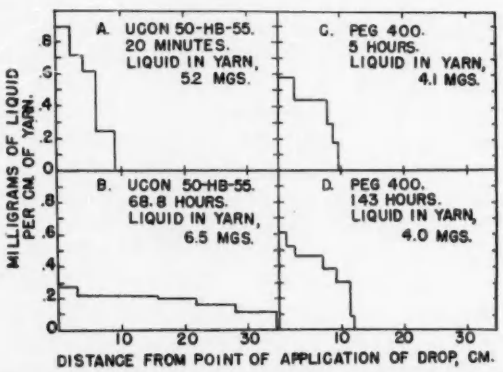
A. UCON 50-HB-55. 20 MINUTES. LIQUID IN YARN, 5.2 MGS.
C. PEG 400. 5 HOURS. LIQUID IN YARN, 4.1 MGS.
B. UCON 50-HB-55. 68.8 HOURS. LIQUID IN YARN, 6.5 MGS.
D. PEG 400. 143 HOURS. LIQUID IN YARN, 4.0 MGS.
MILLIGRAMS OF LIQUID PER CM. OF YARN.
DISTANCE FROM POINT OF APPLICATION OF DROP, CM.

Fig. 8. Distribution of Ucon 50-HB-55 and polyethylene glycol 400 in cotton yarn.

Figure 7 shows a series of similar plots in the system PEG 400–loose nylon yarn; this is a system of appreciable but not excessive contact angle hysteresis. Figure 7A shows the distribution just before the droplet disappeared at the origin and Figure 7B shows the movement over the next 114 hr. The line density has been reduced from the high original value of 0.04 to a value of about 0.03 over a plateau range which extends outward for about 20 cm. from the origin. After another 380 hr. has elapsed (Figure 7C), this distribution has not changed substantially.

A more exaggerated example of this effect is shown in Figure 8. Figures 8A and B show the line density distribution in the low-hysteresis Ucon 50HB55–cotton system in the limited reservoir range, immediately after the drop has disappeared, and about 68 hr. later. During this interval the liquid front has advanced to a point three times as far from the origin and the line density has dropped correspondingly, indicating a migration from the larger to the smaller interfiber spaces. Figures 8C and D show similar distribution curves for the high-hysteresis cotton–PEG 400 system. After the drop has disappeared and the limited reservoir range is reached, very little further wicking or interfiber migration takes place.

Summary

Wicking rates in a series of liquid–yarn systems were measured under such conditions that the effect of gravity was negligible. The results could be graphed as a series of straight lines having the form $s = kt^{\frac{1}{2}}$, where s is distance traveled by the liquid front and t is time; k in this equation is proportional to the set of factors

$$\left(\frac{\gamma r \cos\theta}{\eta}\right)^{\frac{1}{2}}$$

where γ is the surface tension and η the viscosity of the wicking liquid, θ is the contact angle of the liquid against the fiber substance, and r is an "equivalent capillary radius." The r of a yarn is considered proportional to the square root of the cross-sectional area of the interfiber spaces. This relationship between r and the open cross-sectional area was verified by measuring wicking rates in filament nylon yarns of known interfiber spacing. In crenulated viscose filament yarns, where the interfiber spacings are larger than calculated, the wicking rates were abnormally high.

In identical yarns having the same value of r, the wicking rates of a group of liquids were found to fall in the same order as the K values, which are defined as the values of the quantity $(\gamma \cos\theta)/\eta$. This relationship was found to be valid for a wide variety of liquids in nylon, viscose, cotton, and wool yarns.

The wicking pattern was measured of single liquid droplets placed on a horizontal yarn. It consists of two distinct regions:

1. The region before the drop sinks completely into the yarn. This is called the "unlimited reservoir" region or period, during which the equation $s = kt^{\frac{1}{2}}$ expresses the advance of the liquid front.
2. The region or period after the drop has sunk into the yarn. This is the "limited reservoir" region in which the liquid decelerates and finally ceases to move. The ultimate length of this limited reservoir region in yarns of constant r differs from liquid to liquid. It is shown that this difference in length depends on the contact angle hysteresis of the fiber–liquid system. In systems of high contact angle hysteresis the limited reservoir region is short.

The distribution of wicking liquid within the yarns was measured in both the unlimited and limited reservoir regions. The distribution pattern in the limited reservoir region also varies from liquid to liquid and depends on the contact angle hysteresis.

Acknowledgment

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Part III: The Behavior of Liquids on Single Textile Fibers

Introduction

It is well recognized that the wicking of liquids in a textile fabric takes place mainly through a capillary system composed of the individual fibers in more or less parallel array. It can also be demonstrated that the simplest and most fundamental system of this type (discussed later in this paper) consists of two parallel fibers separated by a critical distance below which the capillary forces will have a tendency to cause liquid flow in the interfiber channel. For a thorough understanding of the wicking process, however, it is necessary to describe the capillary behavior of a liquid in contact with single isolated textile fibers. Such a description is particularly valuable when the total mass of wicking liquid is relatively small, as in the case of a single droplet of liquid coming in contact with a fabric. This paper describes the observed behavior of several representative organic liquids on various textile fibers and discusses this behavior in terms of capillary theory. Methods for measuring the contact angle and contact angle hysteresis of liquids against single fibers are also described.

Droplets on Single Fibers

The single fiber to be studied was suspended horizontally under sufficient tension to hold it taut and was placed in the field of view of a projection microscope. A droplet of liquid was placed on the fiber and observed for evidence of spreading along the fiber shaft. Small droplets of liquid may be placed on fibers by shooting them from the end of a hypodermic syringe needle at the fiber. This can be accomplished by drawing a small bubble into the syringe needle, then tapping the piston of the syringe. It is more convenient, however, to transfer liquid to the fiber under observation by means of another fiber. The conditions for this method of transfer of liquid are that the conveying or feeder fiber be smaller in diameter (at the point of transfer) than the receiving fiber and that the contact angle of the liquid against both fibers be less than 90°. As an example, a single fine glass fiber, conveniently cemented to a handle, was dipped into Ucon 50HB55 and withdrawn rapidly so that it bore a few droplets of liquid. This loaded glass fiber was touched to a wool fiber of considerably greater diameter. The liquid adhered to the wool fiber and remained there when the glass fiber was withdrawn. By repeating this operation increments of liquid could be added to the liquid already present on the wool fiber, thus building up the droplet on the wool fiber as much as was desired. To withdraw liquid from the droplet on the wool fiber it was necessary only to touch the droplet with a fiber (or other object) having a larger diameter than the wool fiber and a contact angle against the Ucon not substantially greater than the Ucon–wool contact angle. A nylon bristle was convenient for this purpose.

A variety of liquid–fiber systems were studied. The liquids and fibers used included the following.

Liquids

Dibutyl butyl phosphonate, diethyl sebacate, Ucon 50HB55, 2-anilinoethanol, oleic acid, polyethylene glycol 400, diethylene glycol, castor oil, Nujol (hydrocarbon), and Kel-F oil (fluorocarbon) were used. All these liquids are characterized by low volatility at room temperature. For easier observation they were colored with 0.5% of an inert oil-soluble red dye.

Fibers

Wool, nylon, glass, viscose, and acetate rayon were used. After equilibrium had been established, there were three different situations noted, depending upon the liquid–fiber system. In one situation, observed with viscose and acetate rayon fibers and all of the liquids tested, the drop slowly shrank over an interval of hours, appeared to spread out over the fiber, and eventually disappeared. Although slow, the spreading process appeared to be continuous.

The second situation, noted with liquid–fiber systems (excluding viscose and acetate) where the contact angle was small, is illustrated in Figure 1. In this situation, the liquid entirely surrounded the fiber and did not spread, but formed a bead with the fiber passing through its center. This bead form is hydrodynamically stable and has the geometrical form of an unduloid. This is a figure of revolution formed by rotating an elliptical cycloid (the profile of the bead) about its axis (the axis of the fiber) [1]. It meets the Laplace requirement for stability, namely that at all points over the liquid–air surface the sum of reciprocals of the two principal radii of curvature,

$1/R_1 + 1/R_2$, is a constant. It is noteworthy that the droplet of liquid, having assumed this shape, has no tendency to spread macroscopically over the surface of the fiber even though the contact angle may be zero. This situation is startling when first observed, since it is well known that on a flat solid surface (where the liquid–air surface assumes the form of a spherical zone) a zero contact angle is tantamount to indefinite spreading. It is possible and even probable that a monolayer forms over the surface of the fiber by a two-dimensional diffusion process starting at the air–fiber–liquid boundary line. But no capillary pressure exists in this configuration analogous to the pressure which causes the indefinite spreading of a droplet on a flat plate in a zero contact angle system. Furthermore, the equilibrium zero contact angle at the air–fiber–liquid boundary line has already been achieved. There is therefore no tendency for the shape of the air–liquid interface near this boundary line to change. The unduloid shape of the drop in Figure 1 is a stable equilibrium shape of minimum total interfacial free energy despite the fact that the contact angle at the air–solid–liquid boundary line is zero. It is noteworthy that an extended thick film of liquid placed on the surface of the fiber will also contract and "ball up" to an unduloid or break up into several unduloids when the axial length of the tubular film is substantially greater than three times its diameter. The same forces cause this phenomenon as cause a long cylinder of unsupported liquid to break up into drops.

The third situation was observed with liquid–fiber systems (excluding systems with viscose and acetate fibers) in which the contact angle was high. In this situation, the droplets did not entirely surround the fiber. The extremely large droplets of this type approached the sphere in form (Figure 2A). The smaller droplets exhibited forms resembling clamshells attached to the fibers (Figures 2B and 2C).

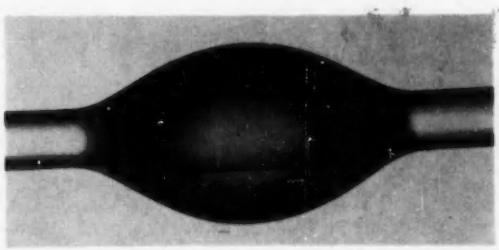


Fig. 1. Diethyl sebacate droplet on nylon filament. Unduloid form typical of low contact angle.

In all the drops of this type, a line of contact of the liquid surface with the fiber surface could be seen. The clamshell droplet was observed with all liquids used on Teflon fiber and with many liquids on wool. This clamshell form is also stable and fulfills the Laplace curvature requirement.

Whether a liquid droplet forms an unduloid or a clamshell depends not only on the contact angle but also on the volume of the liquid relative to the volume per unit length of the fiber. Liquids of zero contact angle should not theoretically form stable clamshell drops, and none have been observed in these studies. Figure 3, for example, shows the typical unduloid formed by a small droplet in a zero contact angle system. In systems having a contact angle greater than zero it is evident that a sufficiently small droplet

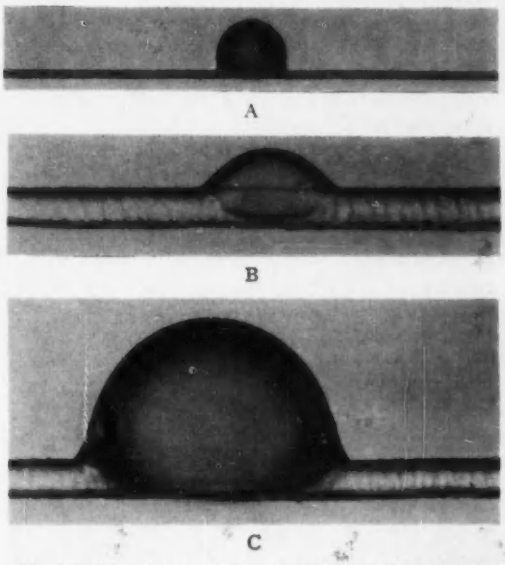


Fig. 2. Clamshell droplets. (A) Ucon 50-HB-55 droplet on Teflon filament; large droplet of nearly spherical shape. (B) Polyethylene glycol 400 droplet on wool; typical shape of small droplet. (C) Large polyethylene glycol 400 droplet on wool; typical shape of intermediate size droplet.

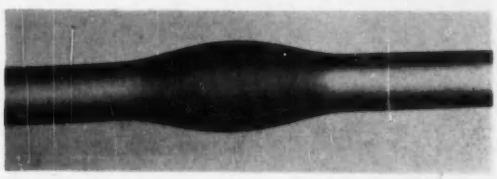


Fig. 3. Typical unduloid formed by small droplet with zero contact angle; dibutyl butyl phosphonate on nylon filament.

must always form a clamshell. Larger droplets can under favorable circumstances form unduloids, provided the contact angle is not too high. Figure 4 shows two views of a droplet of Ucon 50HB55 on a wool fiber. One shows the unduloid form while the other shows the clamshell form. By careful manipulation (using the needle whose tip appears in the clamshell picture) one form could be changed to the other. In this case the contact angles (in the range of 5° min. receding and 35° max. advancing) and the ratio of drop volume to fiber diameter are such that both forms are relatively stable and persist if left undisturbed.

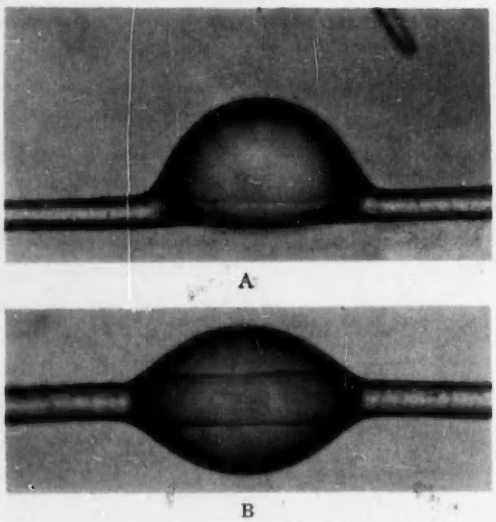


Fig. 4. Ucon 50-HB-55 droplets (two forms) on wool. (A) Clamshell form, (B) unduloid form.

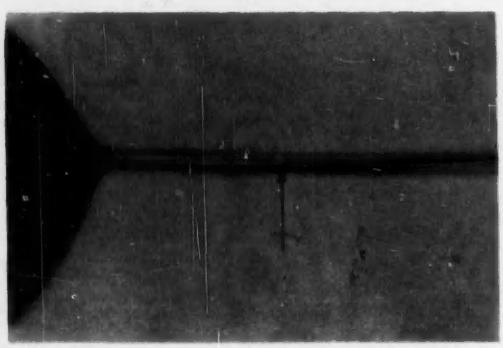


Fig. 5. Groove in fiber, partially filled by migrating liquid. Arrow points to liquid front in the groove. Anilinoethanol on viscose filament.

The influence of gravity in fiber–liquid systems of this size and description is very small compared to the influence of the surface and interfacial forces. The droplet of Figure 1, for example, has an average radius of curvature of about 30 μ. If the liquid has a surface tension of 30 dynes/cm. the capillary pressure on the interior of the drop is, according to the well-known Laplace formula, approximately 20,000 dynes/cm.^{2} This corresponds to a total upward force of about 1 mg. or 1000 μg. exerted against the under side of the droplet. The droplet itself weighs approximately 0.15 μg. Thus the total gravitational force tending to produce distortion is only about 1/6,600 as great as the force tending to keep the droplet in its unduloid form.

When a droplet of nonvolatile liquid of low contact angle was placed on a fiber of apparel-type viscose rayon it was observed to diminish in size rather slowly. Closer examination indicated that the liquid was moving outward away from the droplet along the fiber surface. When highly colored liquid was used, it could be observed that the liquid was flowing in the surface grooves or crenulations which characterize this type of fiber. From the known dimensions of these grooves it can be calculated that they will act as capillary channels for liquids of low contact angle. Figure 5, a photo of a large uncolored liquid drop, clearly shows the liquid advancing in a deeper-than-average groove along the surface of a viscose fiber.

To check the fact that the liquid migrated along the viscose fiber surface only because of and only by means of the crenulations, several single fiber–liquid droplet systems were examined as follows. The fiber was mounted taut across a gap of about 3 cm., slightly inclined from horizontal. At the high side of the gap the fiber was pressed firmly against a sheet of absorbent paper so that any liquid transferred would be absorbed by the paper and could be ob-

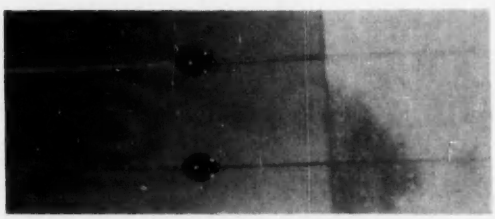


Fig. 6. Creep of liquid along fibers. Top fiber: wool, not crenulated. Liquid did not creep along fiber. Bottom fiber: viscose filament, crenulated. Liquid crept along fiber, staining paper at right.

served visibly. It was shown in preliminary work that as little as 0.1 μg. of liquid could be detected with certainty in the absorbent paper. A drop of the dyed liquid was applied to the fiber a few millimeters from the paper. The whole system was observed under a microscope of long working range. Combinations of the following fibers with the following liquids were observed.

Fibers

Wool, cotton, glass, crenulated viscose, and smooth-surfaced viscose were used.

Liquids

Diethyl sebacate (DES), anilinoethanol (AE), Ucon 50HB55, and dibenzylamine were used.

The only fibers which showed transfer by creep were the crenulated viscose fibers. These showed appreciably rapid and continuous transfer with each of the test liquids.

These results are illustrated in Figure 6, which shows a crenulated viscose fiber and a wool fiber mounted in the manner described above. Liquid from the droplet on the viscose fiber moved along the fiber and produced a stain in the paper. This did not occur with the wool fiber.

No proven example of creep of liquid along the surface of an uncrenulated fine textile fiber has as yet been observed.

Droplets on Two Parallel Fibers

The simplest model of a yarn acting as a capillary wicking system consists of two parallel smooth-surfaced fibers of approximately circular cross section. It has been pointed out in another publication [3] that such a system can act as a capillary when one end is dipped vertically into a reservoir of liquid. In the present work the behavior of liquid droplets was observed on pairs of parallel fibers mounted horizontally in order to minimize the effects of gravity. The fibers were stretched across separate frames which were so arranged that the distance between the fibers could be controlled. The liquid droplets were applied and their behavior was observed by means of a low-power long-range microscope.

The first observations were made with coarse wool fibers about 3 in. long and 50–70 μ in diameter. The fibers were set parallel to each other and about three fiber diameters apart. A large droplet of Ucon 50HB55 was placed across the fibers. It assumed the approximate shape of an ellipsoid of revolution pierced by the two fibers, as shown in Figure 7A, and showed no tendency to wick out between the fibers. When the fibers were moved closer to each other, so that they were separated by a distance of approximately one fiber diameter, the first droplet of liquid which was added collected between the

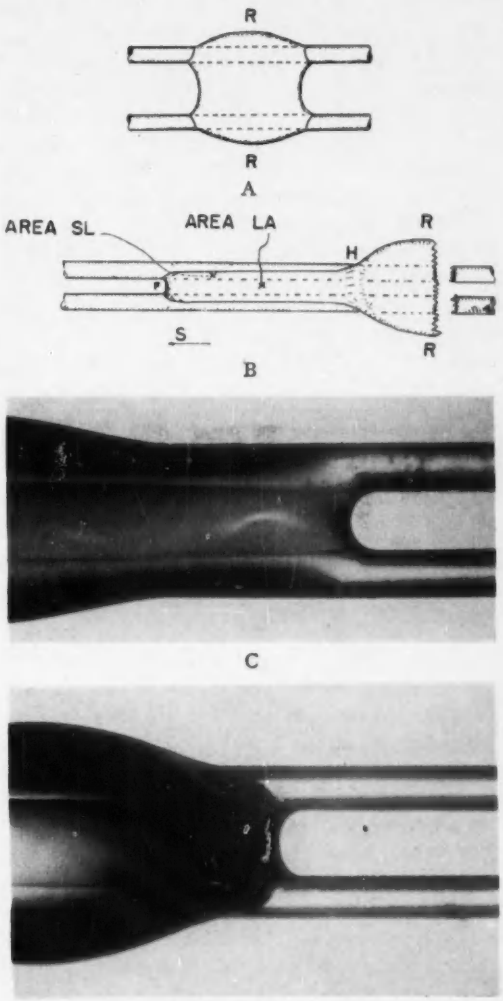


Fig. 7. Droplets of Ucon 50-HB-55 on parallel fibers. (A) Droplet on widely spaced fibers. Does not advance. (B) Droplet on closely spaced fibers, advancing along fibers. (C) Ocon 50-HB-55 droplet on nylon. Liquid partially advanced between two fibers. (D) Polyethylene glycol 400 droplet on nylon. Liquid static between two widely spaced fibers.

fibers as described above. On adding a second droplet the liquid started to wick out between the fibers, as shown in Figure 7B. If the total quantity of liquid was not too large and the fibers were not too close together, the system could by careful manipulation be brought to an apparent equilibrium state with the liquid front F not too far from the bulk of the droplet R. A situation of this type is shown in Figure 7C, Ucon 50HB55 on a pair of nylon fibers. When the fibers were spaced very closely (less than about 0.6 fiber diameters apart) the liquid wicked out rapidly, completely depleting the droplet reservoir R. There was also a strong pressure exerted by the wicking liquid tending to draw the parallel fibers closer to each other.

When polyethylene glycol 400 or diethylene glycol was used as the wicking liquid, the fibers had to be brought very close to each other (about 0.1–0.2 fiber diameters apart) before the spontaneous wicking with complete depletion of R took place. These liquids show a contact angle in the range of 40° against wool.

Similar observations were made on pairs of nylon fibers using liquids of zero contact angle and contact angle higher than zero but much less than 90°. The effects were similar to those observed on wool fibers. The liquids of higher contact angle did not wick until the fibers were spaced quite close to each other.

Two systems comprising Teflon fibers were examined. In one of these the liquid was Ucon 50HB55 and the system had a contact angle slightly less than 90°. When the fibers were held in contact with each other, the Ucon moved out slowly in the notch or groove formed between the fibers. When diethylene glycol was used as the liquid, the contact angle appeared to be slightly greater than 90°. No outward movement of the liquid occurred in this system, even when the fibers were held in contact with each other.

The behavior of these systems can be accounted for theoretically, in relatively simple terms, using the thermodynamic treatment described previously by two of the authors [4]. According to this treatment, wicking will occur when dF/ds is negative, F being the free energy of the system and s the distance traveled by the liquid front in the direction away from the reservoir (Figure 7B). Designating the solid, liquid, and gas phases by S, L, and A, and using γ to designate interfacial free energy, the free energy change during wicking is described by the following equation.

$$\frac{dF}{ds} = \frac{d}{ds}(\text{Area } LA)\cdot k_1 + \frac{d}{ds}(\text{Area } SL)\cdot k_2 \quad (1)$$

where $k_1 = \gamma LA$ and $k_2 = (\gamma SL - \gamma SA)$. k_2 is negative in systems where the contact angle is less than 90°. It is only in these systems that dF/ds can be negative and that wicking can take place. It is evident from the geometry of the system (Figure 7B) that the ratio of the magnitudes of d (Area SL)$/ds$ and d (Area LA)$/ds$ depends on how closely the fibers are spaced. Close spacing decreases d (Area LA)$/ds$ while leaving d (Area SL)$/ds$ unchanged, and thereby tends to promote wicking. Equation 1 shows that a decrease in the algebraic value of k_2 will also tend to promote wicking. Since a small negative k_2 value corresponds to a high equilibrium contact angle, liquids of low contact angle will wick at a wider fiber spacing than liquids of high contact angle.

The intermediate situation represented by Figure 7C can have two possible causes. When R (the reservoir droplet) is small any increase in Area SL at F (the liquid front) causes a decrease in Area SL at H (Figure 7B). Thus d (Area SL)$/ds$ might be big enough to make dF/ds negative when R is large, but too small to make dF/ds negative when R is small. Another possibility is contact angle hysteresis in the system. Thus the advancing contact angle at F could be greater than the receding contact angle at H. This would also tend to stop the forward motion of the liquid at F when R became sufficiently small.

The Measurement of Contact Angle in Liquid–Fiber Systems

General Considerations

The term "contact angle" has been used in the literature of surface physics to signify at least two conceptually different quantities. The first is the physically measurable angle between the LA interface and the SL interface in a static liquid–solid–vapor system, regardless of whether or not the system is in stable thermodynamic equilibrium. This angle is measured, according to well-known conventions, in the plane perpendicular to both the LA and the SL interfaces; we shall call this quantity the "physical contact angle." The quantity which we shall call the "equilibrium contact angle" is best defined in terms of the interfacial free energies of the system by Young's equation (or the refined versions of Young's equation corrected for vapor phase effects).

$$\gamma SA = \gamma SL + \gamma LA \cos\theta \qquad (2)$$

This equation essentially defines θ, the equilibrium contact angle at the three-phase line boundary, in terms of the *interfacial free energies* in the immediate neighborhood of the boundary, symbolized by the gammas. It is evident that there can be only one value for equilibrium θ for any system under fixed conditions of temperature, pressure, etc.

Physical θ does not necessarily coincide with equilibrium θ, for the reason that all static or resting systems are not necessarily in stable thermodynamic equilibrium. Practical systems may be static because they are in a potential trough above the lowest potential trough characteristic of stable equilibrium. This is one of the reasons why physical θ may vary, depending on the history of the system.[1]

We can frequently manipulate a system so that, after it has come to rest, physical θ has a higher or a lower value than it would have had without any special manipulation. The highest static value of physical θ which we are able to achieve by prior manipulation of the system we shall call the "advancing contact angle." The corresponding lowest achievable static value of physical θ we shall call the "receding contact angle."

It should be noted that when physical θ is known to be equal to equilibrium θ, measurements of physical θ can be used to calculate interfacial free energy values. Much of the excellent and invaluable modern work on surface and interfacial energy relationships is based on this fact.

Direct Observation of the Physical Contact Angle on Fibers

The cleaned fiber was mounted horizontally on a frame and placed in the field of a projection microscope fitted with a camera and a prism-lens combination to allow direct visual observation of the droplet on the fiber. By means of a micromanipulator and a feeder fiber or microsyringe, a droplet of the desired liquid was placed on the fiber. The liquids used in this work were all sufficiently nonvolatile so that the droplets did not change significantly in size during the operations described. The contact was made carefully so that the liquid advanced by its own capillarity (rather than by applied mechanical force) along the fiber to its final position. The system was examined carefully to make sure that the silhouette of the droplet and fiber showed the true physical contact angle, i.e., that the silhouette coincided with the exact plane in which the contact angle should be measured. This was no particular problem with well-shaped unduloid droplets; it was a considerable problem with clamshell droplets. Unless the fiber was so mounted that it could be rotated, it was often necessary to apply several droplets before one was obtained which presented a silhouette of the correct plane. The image was then projected on a paper screen and the physical contact angle was traced. Alternatively, a picture of the system was made with either a standard camera or a Polaroid camera, and the contact angle was measured on the print. This angle obtained in this manner was a "tentative advancing contact angle." Several droplets were prepared and photographed in this manner.

After being measured or photographed, the droplets were allowed to sit on the fiber undisturbed for 2 or 3 hr. and were then measured a second time to see if the contact angle had diminished. If it had diminished, the droplets were allowed to remain a further period and were then measured a third time. The highest value of those contact angles which remained constant over a 2–4 hr. period was arbitrarily taken as the advancing contact angle. If the tentative advancing contact angle mentioned above did not diminish on standing, a further increment of liquid was added to the droplet already on the fiber. This had the effect of temporarily increasing the inclination of the LA surface to the SA surface, so that the liquid had to advance along the fiber to achieve a new tentative advancing contact angle. The periodic angle measurements with intervening time lapses were then repeated to ensure that a reasonably static advancing contact angle was achieved.

Figures 8A and 8B show two pictures of the same droplet taken 2 hr. apart. 8A shows a contact angle (on the right side) of 64° and 8B a contact angle of 56°. The angle did not diminish further over the next 4 hr., and 56° could therefore be accepted as an advancing contact angle for this system.

To measure the receding contact angle, liquid was withdrawn from the droplet used to determine the advancing contact angle (droplet of Figure 8B). This can be done by touching a coarser fiber or rod,

[1] The variation in physical θ is generally referred to as contact angle hysteresis. Two other well-recognized causes for contact angle hysteresis are physical roughness of the solid surface [4] and adsorption of the liquid at the solid–liquid interface, thus changing the character of the fresh SA interface which becomes exposed when the liquid recedes.

or the tip of a fine syringe needle, to the top of the droplet and then withdrawing carefully. The bulk of the liquid will stick to the coarse withdrawing implement and will eventually separate, leaving a smaller droplet on the fiber. The appearance of the droplet while being withdrawn is shown in Figure 9A; the appearance of a typical residual droplet left on the fiber is shown in Figure 9B. The contact angle of this residual droplet is measured shortly after it is formed, and again at intervals of 2 hr., during which time it may increase. The minimum static angle observed after several trials is taken as the receding contact angle for the system; in the PEG 400–wool system of Figure 9B it was 18°.

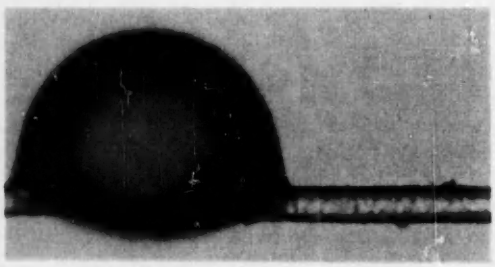
With careful focusing and manipulation it is possible to obtain sharp, reproducible, and easily measured contact angles. Figures 10A and 10B show advancing and receding contact angles (40° and 10° respectively) of PEG 400 on a smooth-surfaced viscose monofilament. Figure 10C shows the typical appearance of a zero contact angle system, in this case oleic acid on smooth viscose monofilament. The angles are most conveniently measured by laying a ruler on the background of the picture opposite the profiles of liquid and fiber, with just a thin line of white background showing between the ruler and the dark profile. Lines are ruled parallel to the fiber profile and to the liquid profile near the three-phase boundary line. By application of this procedure to Figure 10C, it becomes evident that there is no point of discontinuity in the profile; i.e., the physical contact angle is zero. In Figure 10B, however, the point of discontinuity becomes quite sharp by the ruler technique, even though it might not be easily apparent to the unaided eye.

The Wilhelmy Method [2]

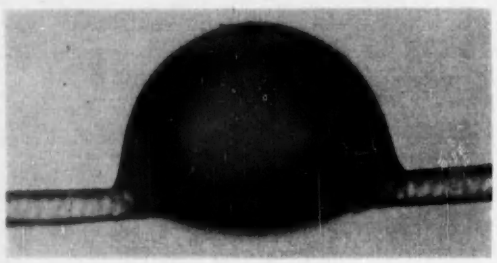
According to the well-known formula of Wilhelmy the pull F exerted on a solid rod inserted into a mass of liquid is expressed by the formula

$$F = p\gamma \cos\theta \qquad (3)$$

where p is the perimeter of the rod along the three-phase boundary line, γ is the surface tension of the liquid, and θ is the contact angle of the system. The theory is by no means rigorously worked out, and

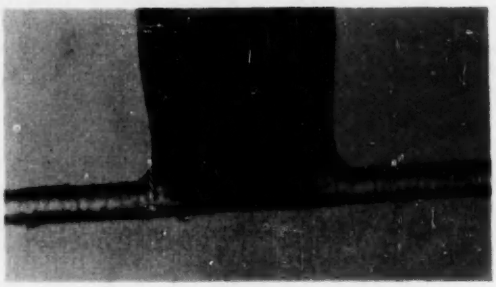


A



B

Fig. 8. (A) PEG 400 droplet on wool fiber, immediately after droplet was placed on fiber. Contact angle, 64°. (B) Same droplet as in Fig. 8A 2 hr. after placing droplet on fiber. Contact angle, 56°.



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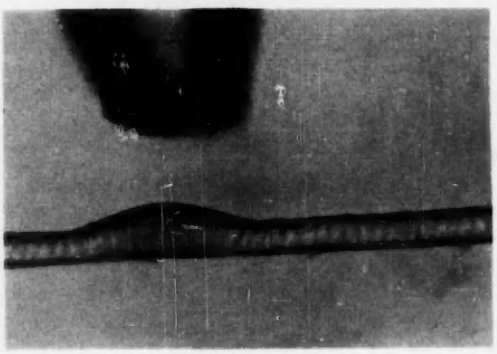

B

Fig. 9. Withdrawal of polyethylene glycol 400 from wool fiber. (A) Appearance of droplet of Fig. 8B during withdrawal of liquid. Note lowered contact angle. (B) Residual droplet after most of the liquid is withdrawn. Note low "receding" contact angle.

some authorities refuse to accept the validity of Equation 3 except when θ is zero and $\cos\theta$ is therefore unity. For purposes of the present discussion we propose that Equation 3 *is* valid for all values of θ provided that F is measured under static conditions (i.e. with the system not in motion) and that θ is interpreted strictly as a *physical* contact angle, not as an equilibrium contact angle.

If the rod has a circular cross section and the plane of the three-phase boundary line is perpendicular to the rod's axis, p becomes equal to $2\pi r$, where r is the radius of the rod. To apply this formula for finding the contact angle of a liquid on a fiber, it is necessary to dip the fiber in the liquid and measure the pull on the fiber. This involves weighing the partly submerged fiber and making appropriate corrections for the weight of the unsubmerged portion and the buoyancy of the submerged portion of the fiber. Since the pull on a single fiber is too small for convenient measurement, the pull on several fibers must be measured simultaneously. A frame or zither bearing 50 evenly spaced fibers, each in the form of a U, was prepared. This allowed the pull on 100 fiber shafts to be measured simultaneously. The construction of this frame is shown in Figure 11. Since the fibers must be spaced far enough apart to avoid capillary action in the interfiber spaces, it is necessary to have some sort of spacing device. A fine-tooth comb with the teeth sawed off nearly to the root was found satisfactory. Two of these formed the main bars or side pieces of the frame. They were joined by two pillars, P, made from stiff steel wire. A very light scratch mark was placed on each pillar at a fixed distance (conveniently 1 cm.) from the bottom bar. A thread, T, which served to hang the frame from the hook H of an analytical balance completed the assembly.

In making the measurement of pull, the bare frame is first immersed in the test liquid exactly to the mark on the pillar and is weighed. This affords a correction for both frame buoyancy and for the Wilhelmy pull on the vertical columns of the frame. The frame is dried and is then strung with the fibers and weighed in air. It is then immersed to the mark

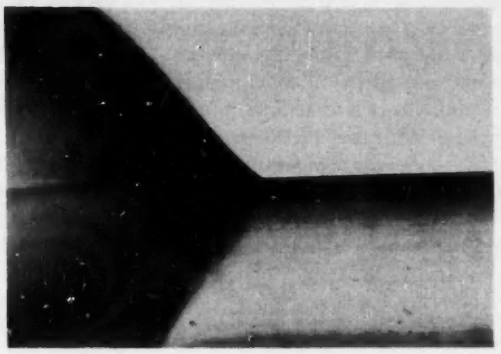

Fig. 10. Contact angles on smooth-surfaced viscose filament. (A) Advancing contact angle of polyethylene glycol 400 on smooth-surfaced viscose. Contact angle, 40°. (B) Receding contact angle of polyethylene glycol 400 on smooth-surfaced viscose. Contact angle, 10°. (C) Advancing contact angle of oleic acid on smooth-surfaced viscose. Contact angle, zero.

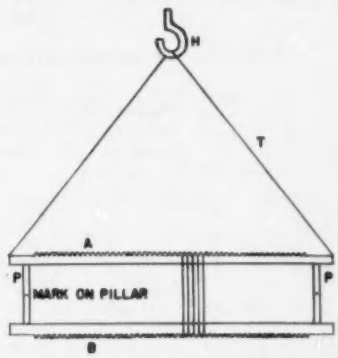

Fig. 11. Zither or frame for the Wilhelmy method of determining contact angle.

and weighed again. The frame is then cleaned, dried, and given a final weighing. In stringing the frame with staple fibers, each fiber is looped around a notch in the bottom bar and is then tied taut over the top bar. Filament fibers can be wound continuously around the bars.

The fact that 100 measurements are being made simultaneously gives an automatic average of the fiber perimeter factor. It also takes care of local point-to-point variation of the physical contact angle over the surface of the fiber.

The illustrative measurements reported herein were all made with a clean sample of carpet wool. The individual fibers averaged about 17 cm. in length. To calculate an average perimeter for these fibers, exactly 10 m. of fiber was measured out and then weighed. From this measurement and the known density of wool (1.33), the average perimeter was calculated. The total error in both length and weight measurements was estimated at 0.6%.

In making a measurement the loaded frame was immersed to the mark on the pillar and a weighing was made, taking care not to withdraw the frame even to the slightest extent during the adjustment of weights. Thus an "advancing" pull value was obtained. In exactly the same way a receding pull value was obtained after starting to withdraw the frame. Several such weighings were made with each fiber–liquid pair to obtain average values. The replicability of the measurements was usually quite good. It was found that a single threaded zither could be used many times over. One zither could even be used in different liquids if it were cleaned carefully between runs and if the liquids did not swell or penetrate the fibers or the frame bars.

A representative set of data and calculations is given in Table I, and the contact angles of several liquids measured on wool fibers are shown in Table II. The range of pull values in this table is slightly greater than the range obtained with smooth-surfaced

TABLE I. Determination of Contact Angle by the Wilhelmy Method

Example: Polyethylene glycol 400. Density, 1.13 g./cm.³ Surface tension, 49 dynes/cm. 100 wool fibers. Vol. submerged wool, 1.44 cu. mm. Total circumference of fibers, 1.25 cm.

1.	Weight of bare zither (in air)	1018.8 mg.
2.	Weight of bare zither submerged to a depth of 1 cm.	439.3
3.	Difference: decrease in weight when bare zither was submerged	579.5 mg.
4.	Calculated weight of liquid displaced by wool on loaded zither when submerged	1.6 mg.
5.	Calculated total decrease in weight on immersion of loaded zither, if no pull	581.1 mg.
6.	Weight of loaded zither (in air)	1043.0 mg.
7.	Calculated weight of loaded zither when submerged to 1 cm., if no pull = Line 6 minus Line 5	461.9 mg.
8.	Observed weight, loaded zither in the liquid	507.0 mg.
9.	Total pull = Line 8 minus Line 7	45.1 mg.
10.	Pull per unit line of contact of liquid surface on wool = total pull/total circumference of fibers	36.1 mg./cm.
11.	Pull/cm. line of contact in dynes	35.3 dynes/cm.
12.	Cos θ = pull per cm./surface tension	.721
13.	Contact angle calculated from pull = $\cos^{-1}$.721	43.9°

TABLE II. Contact Angles of Liquids Against Wool, Determined by the Wilhelmy Method

Liquids	Surface tension, dynes/cm.	Pull measured after	No. of measurements	Pull on wool, dynes/cm. Range	Pull on wool, dynes/cm. Average	Calculated contact angle,° Range	Calculated contact angle,° Average
95% Ethyl alcohol	$22.4^{21°}$	Advanc'g	6	23.6–24.0	23.7	—	0
		Reced'g	5	23.7–24.0	23.9	—	0
Diethylene glycol	$48^{25°}$	Advanc'g	4	35.3–36.2	35.7	42.7–41.1	41.9
		Reced'g	3	49.3–49.4	49.3	—	0
Oleic acid	$32.5^{20°}$	Advanc'g	5	32.0–33.2	32.4	8.5– 0	4.5
		Reced'g	5	33.6–34.1	33.9	—	0
Polyethylene glycol 400	$49^{27°}$	Advanc'g	5	32.4–34.4	33.5	47.9–45.5	47.6
		Reced'g	11	41.3–43.7	42.6	32.5–26.7	29.6

nylon and viscose fibers. The high pull obtained with ethyl alcohol may be due to penetration of the fiber or possibly to condensation on the fiber above the liquid level. Pulls of 1 dyne/cm. (or even slightly more) higher than theoretical were, however, also obtained in a few other instances.

Since $\cos\theta$ changes very slowly in the region where θ is small, a small error in the pull measurement leads to a large error in the calculated value of θ. This is an inherent weakness of the method. There is little doubt, however, that the procedure described above can be refined for considerably greater precision. Even at the present level of precision it is a valuable supplement to visual or photographic observations, particularly in systems of high hysteresis having contact angles in the range of about 30–70°.

Summary

The physical behavior of small single droplets of organic liquids on a variety of textile fibers was examined. The selected liquids did not penetrate, react with, or swell the fiber; the droplets weighed in the range of 1 μg. On smooth-surfaced fibers of approximately cylindrical cross section the droplets formed either unduloids (surrounding the fiber) or clamshell-shaped beads clinging to one side of the fiber. Droplets having a contact angle of zero always formed unduloids, and those having a contact angle over about 60° always formed clamshells. At intermediate contact angles either form could be obtained, depending on the ratio of the droplet volume to the fiber diameter.

Liquids of low contact angle applied to viscose and acetate rayon fibers having longitudinal surface grooves spread outward from the original droplet. The grooves acted as capillary conduits for this liquid migration.

A liquid droplet of low contact angle applied to a pair of parallel fibers either maintained its original pierced bead form or wicked out between the fibers while tending to draw them together. For each liquid–fiber system there was a critical distance between fibers below which wicking occurred. The critical distance decreased as the contact angle increased.

Methods for measuring the contact angle of liquid droplets on fibers by direct observation are presented in detail. A method for measuring the fiber–liquid contact angle by a Wilhelmy method is described. The fibers are fastened to a light frame and the pull on 100 fiber shafts is measured. Both advancing and receding contact angles can be measured with good precision.

Acknowledgments

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2. Collins, G. E., *J. Textile Inst.* **38**, T73–77 (1947) has described a Wilhelmy method for measuring contact angles of liquids on fibers which is very similar, except in detail, to the method herein described. Collins uses only two fibers in his frame and reads the pull by means of a microbalance sensitive to 0.003 mg. The 100-fiber frame we use gives an average pull value and does not require precise determination of individual fiber perimeters.
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The Stability to Laundering of Fabrics Made from Cellulosic Fibers

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Abstract

The laundering shrinkage of fabrics made from cellulosic staple fibers can be conveniently broken down into three types: first, fiber relaxation type, due to relaxation of strains imposed on fibers during processing; second, fabric relaxation due to fiber and yarn swelling which results in crimp adjustment and subsequent shrinkage; and third, "felting" or "progressive" type due to fiber movement. The fabric relaxation type of shrinkage is apparently dependent upon the degree of fiber swelling in water, while the felting or progressive type of shrinkage is primarily dependent upon the ease of stretch of the fibers in the wet state. Fibers with a tenacity at 5% extension of 0.6 g./den. make fabrics which do not suffer from "felting" or "progressive" shrinkage. Yarn and fabric geometry also affect both shrinkage types. In general it can be said that yarn and fabric constructions which give more bulk or less compactness will have less of the relaxation type of shrinkage potential. For felting type shrinkage, it is apparent that factors which facilitate relative fiber movement under severe water agitation will result in greater felting shrinkage. Loose fabric construction and weave type, high yarn twist with warp and filling of similar twist direction, finer denier, and longer staple length all tend to increase the felting potential of cellulosic staple fabrics.

Introduction

In order to produce and develop cellulosic fibers with greater inherent resistance to laundering shrinkage, it became evident that a more fundamental knowledge of the mechanics of fabric shrinkage during laundering had to be obtained. A program was undertaken to study the effects of fiber, yarn, and fabric properties on shrinkage in laundering. The first part of this study was a survey of the literature on the subject of laundering shrinkage in general.

Types of Shrinkage

An initial survey of the literature, together with our experience to date on this subject, made it apparent that the general problem of shrinkage in viscose fabrics may be broken down into three types, which may occur separately or together in any fabric. The importance of each type depends on the characteristics of the fiber, the construction of the yarn and fabric, and the processing history of the fabrics.

These three classifications are shrinkage due to fiber and yarn swelling, shrinkage due to relaxation of fiber stresses, and felting shrinkage or progressive shrinkage due to movement of individual fibers within the yarns and fabrics.

In the absence of dried-in strains on fibers, they do not shrink on wetting. Meredith [14] showed (see Table I) that previously unstrained nylon, cotton, wool, silk, and viscose rayon fibers all increase in length as well as in diameter when wet.

In spite of this increase in fiber length on wetting, however, the fabrics into which the fibers are made almost invariably become smaller in area. The best account of the mechanism involved appears in a paper by Collins [5].

In this paper Collins points out that although shrinkages in cotton fabrics of the order of 10% or more are common, they cannot be attributed entirely to shrinkage of the fibers on wetting. He points out that when fabrics are subjected to tensile loads, the fabric stretches first, followed by the yarn; finally, the last link in the chain, the fiber itself, is stretched when the load approaches the breakdown value. In most cases of shrinkage in cotton goods, it is safe to say that actual fiber shrinkage is not more than 2% and is generally less than 1%.

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Collins then goes on to consider the shrinkage of the yarn. He points out that although the effect of fiber length change is small, the effect of change in fiber diameter is much greater. If the fiber diameter increases by 14% on wetting and there is no free interfiber space in the yarn, then the yarn diameter must increase by 14%. Having established that the diameter of the yarn increases on wetting, Collins goes on to show that since the fibers spiral around the yarn and the yarn increases in diameter on wetting, the yarn must either untwist or contract in length if the fibers are to maintain their original length. Since yarns in fabrics are not allowed to untwist, they must contract in length.

However, calculations indicate that when a cotton yarn of 3.7 twist multiplier increases in diameter by 14%, it is not likely to shrink more than 2%, a value very much less than those experienced on cotton fabrics. It is therefore apparent that with cotton, yarn shrinkage is not the prime cause of fabric shrinkage.

It is therefore necessary to look at the structure of the fabric for an explanation of the way in which the major part of fabric shrinkage occurs in cotton fabric. Figure 1, taken from Collins' paper, demonstrates the manner in which fabric shrinkage occurs. It has been shown that the yarns will increase in diameter when the fabric becomes wet, and if the warp and filling threads were to retain their original spacings, the yarn would have to increase in length or be stretched. Force is necessary to effect such a stretch; in the absence of force, the line of least resistance is taken. This path of least resistance is the moving together of threads, resulting in fabric shrinkage. Calculations from the geometry of cloth structure show that the shrinkages which can result in this way increase as the thread spacing is reduced and became considerably greater than the shrinkages possible due to yarn swelling alone. When the warp and filling threads are very close, some limit to shrinkage is set by jamming, beyond which it is not possible for the threads to be pulled any closer together.

It becomes apparent that, on wetting, the cloth tends to adjust itself from an unstable and strained state to a more stable distribution of crimp between warp and filling. This mechanism of crimp adjustment is governed by the size of warp and filling yarns and the number of ends and picks per inch.

From the above considerations, it is clear that the construction of cotton fabrics may be modified so as to produce fabrics of greater or less shrinkage potential on washing. It appears that the most stable fabrics should be spun from yarns of minimum twist to reduce both yarn shrinkage and swelling to a minimum and should be woven as loosely as possible, with as few weave interlacings as possible.

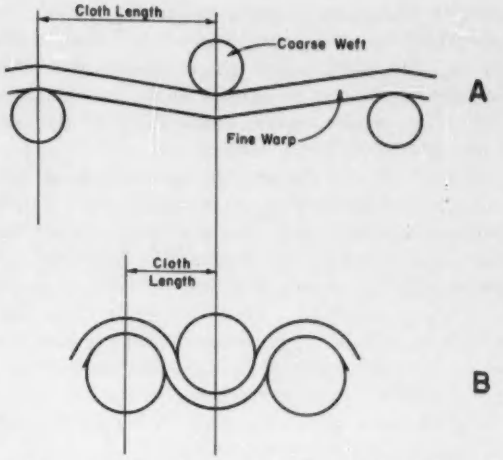


Fig. 1. A geometric explanation of cloth shrinkage (from Collins, "Principles that Govern the Shrinkage of Cotton Goods").

Dorkin and Chamberlain [8] showed that, in the absence of dried-in strains, viscose rayon staple yarns of low twist may extend on wetting. This, together with the large diameter swelling of rayon, suggests that the effect of yarn twist and fabric construction on the shrinkage of rayon fabrics will be greater than on cotton fabrics.

Relaxation of Stresses

It is clear from the previous discussion that, in all fabrics composed of fibers which swell on wetting, a large part of the shrinkage which occurs in washing must be due to rearrangement of crimp in the fabric. It is also clear from the work of Collins that the effect of releasing strains imposed on the fiber during

TABLE I

Fiber	Percentage increase in length	Percentage increase in diameter
Nylon	1.2	5.0
Cotton	1.2	14.0
Wool	1.2	16.0
Silk	1.7	18.7
Viscose rayon	3–5	26.0

previous processing is negligible in the case of cotton, which has a high tensile modulus, both in the wet and dry states. However, it appears likely that this effect will be much greater in the case of fibers with lower tensile moduli, particularly in the wet state, such as wool and viscose.

Marsh [12] says that in many instances the shrinkage of rayon goods may be accounted for by fiber and yarn shrinkage, particularly where stretching has taken place during manufacture. According to Marsh, rayon, unlike cotton, may exhibit up to 9–10% yarn shrinkage. However, apart from this remark by Marsh, the literature appears to be silent on the question of what part of the relaxation shrinkage of fabrics made from fibers which are easily extensible, particularly when wet, is actually due to shrinkage of the fibers on wetting.

Felting Shrinkage or Progressive Shrinkage

In this discussion felting shrinkage is used to describe the phenomenon in which fibers entangle with each other and pull together into denser areas.

Until quite recently it has been believed that wool is the only fiber which felts and, because of the economic importance of the fiber, a large amount of work has been done on the felting of wool over many years.

Munge [15] found in 1790 that, during the fulling process, wool hairs always migrate in the direction of their root ends. He attributed this to their imbricated surface. Ditzel [7] in 1891 showed that free fibers showed no diminution in length during the fulling of a piece of cloth which shrank 16% in length and width. He also established that the wool hairs travelled in the direction of their root ends during fulling.

Arnold [1] confirmed and extended the ideas of Ditzel in 1929 to show that the fibers stretch and move in a similar manner to that in which an earthworm crawls. Shorter [17], on the other hand, described wool cloth as a collection of "self-tightening mechanisms," in which each fiber in the cloth will have places of tight and loose entanglements; hence fiber travel will diminish the distance between the entanglements by drawing them together if the scales are properly orientated. Speakman [18] effectively married these points of view by describing the mechanism as being not unlike an elastic sewing thread which draws up the fabric on recovering from extension.

It seems now to be generally agreed that the three fiber properties which are involved in felting are a directional frictional effect, which makes it possible for the fiber to move or be moved more easily in one direction than the other; ease of extensibility when wet; and power of recovery from extension when wet.

Bogaty, Sookne and Harris [3] carried out a very illuminating study of these factors by studying the elastic and swelling properties of individual wool fibers in a series of organic and inorganic solutions and comparing their single fiber results with the felting characteristics of fiber masses in the same solutions, as measured by changes in the length of pieces of wool top. Their findings are expressed below.

1. Increases in fiber swelling result in increased wool top shrinkage.

2. Fibers in a stiffer state (i.e., fibers with a higher work to extend 20%) appear to felt less than those in the more easily extended state.

3. A high degree of resiliency (ratio of work recovered to that required for 20% extension) is associated with a high degree of felting.

Johnson [11] in 1938 investigated the influence of weave structure on the shrinkage of wool fabrics in fulling. He concluded that the greater concentration of threads in a woven fabric, the less it will shrink; the tighter the weave, the more intersections and fewer long floats, the less the fabric will shrink.

Bogaty, Weiner, Sookne, Cozart, and Harris [4] reached the following conclusions.

1. *Effect of fabric texture.* Three plain woven fabrics were made from identical yarns, varying only the number of picks per inch. Substantial increases in felting occurred as the fabric was made more open.

2. *Effect of yarn twist.* The results indicated a slight improvement in stability to laundering as the single twist increased in a plied yarn. Moderately high twists are required to achieve this effect to any important degree.

3. *Effect of twist direction.* Although they say that with yarns of opposing twist directions in the same plain woven fabric, a more feltable fabric is produced than when the directions of twist in warp and filling are the same, their data suggest that the difference is small.

4. *Effect of type of weave.* Of the various weaves examined, the plain woven fabric appeared to be relatively felt resistant.

They summarize their findings by suggesting that the compactness of the fabric structure, whether due to the number or weight of the yarns or to the nature of their interlacings, is the factor which is basic to the feltability of a fabric; looser structures felt more than tighter structures.

In 1933, Speakman cut Wensleydale wool tops of 13-cm. fiber lengths into 5.5-cm. lengths and made yarns and fabrics from the two lots of fiber. When fulled under identical conditions, the shrinkage was 13.4% with the longer fibers and 6.6% with the shorter fibers, suggesting that fiber length is of great importance to the felting shrinkage of wool fabrics, possibly because the shrinkage caused by contraction of stretched fibers will increase with fiber length, causing a greater tendency to migrate.

Although it is widely stated that wool and other animal fibers are the only fibers which will felt, a type of felting in washing rayon staple fabrics under conditions of severe agitation has been observed; reference to the literature reveals papers by Hill and Kornreich [10] and by Best-Gordon [2] in which the phenomenon of felting has been observed on rayon twill fabrics. Both papers agree that the susceptibility to felting is greater when the twist and twill directions cross than when they do not. Best-Gordon ascribes the phenomenon of felting in rayon to the development of "barbs" on the surface of the rayon under severe mechanical abrasion, the effect being accelerated when the fibers are in a swollen state. Felting on washed fabrics made from types of rayon without the development of barbs has been observed in this laboratory, and although it is agreed that repeated washing of conventional rayon fabrics causes felting and the development of barbs, evidence indicates that the two phenomena can and do exist independently of each other.

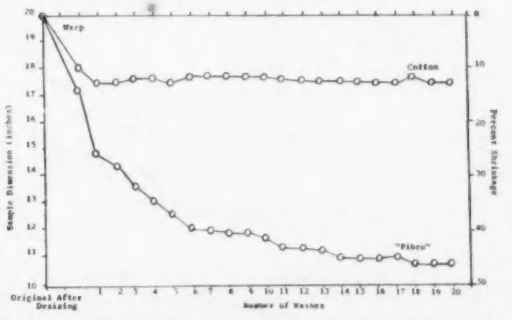


Fig. 2. Laundering shrinkage of cotton and Fibro (Frigidaire automatic washer, 140° F., low washer load).

It is apparent that fabrics made from all fibers which swell in water will shrink because the swelling of the yarns will cause an increase in and re-adjustment of fabric crimp, the amount of shrinkage being, in similar fabrics, proportional to the amount of yarn swelling. It is also apparent that fibers with a low wet tensile modulus are likely to have an additional shrinkage of an indeterminate size, due to relaxation of strains incurred in the fibers during wet processing. In addition to these two mechanisms, wool (and, to a lesser degree, rayon) shrink also by felting. Since rayon has a high degree of swelling, a low wet modulus, and a tendency to felt, it suffers from all three sources of laundering shrinkage.

These types of shrinkage may be illustrated by the typical fabric shrinkage curves of cotton and "Fibro" (viscose rayon staple) in Figure 2. In the case of cotton, an initial large shrinkage due to swelling is followed by a period of stability. Fibro is seen to have an initial large relaxation shrinkage; however, it is succeeded by a further reduction in dimensions accompanied by an increase in fabric thickness and a progressive development of "cover" associated with the movement of fibers relative to each other in the yarns.

The primary objective of this study was to determine the effect of the inherent properties of cellulosic fibers upon laundering shrinkage; however, it was thought that the effect of yarn and fabric properties should be investigated first.

Experimental Method

In order to obtain a more fundamental knowledge of the mechanics of shrinkage occurring in viscose staple fabrics during laundering, an investigation of the following factors was made: the effect of yarn twist and twist direction; the effect of fabric properties (texture, yarn size, fiber denier, staple length, and weave type); and the effect of fiber properties.

In the course of a fiber evaluation program, it was found that particular types of rayon staple fabric exhibited fiber movement under certain washing conditions. Since it would be of benefit to separate the two types of shrinkage, an investigation of washing conditions was started. It became immediately apparent that a light washer load received much more violent agitation than did a heavier load. Experimental work quickly showed that at a heavy washer load (8 lb.), rayon staple fabrics behaved similarly to cotton in that they suffered an initial relaxation shrinkage after desizing and the first wash, then

little change in dimensions and texture during the next nine washes. At a 1-lb. washer load, however, some of the fabrics after an initial relaxation shrinkage underwent a marked and further shrinkage accompanied by the development of a felted appearance. This is illustrated in Figure 3, which shows typical curves at the two washer loads.

At this point it became apparent that the shrinkage at an 8-lb. load could be used as an approximate measure of swelling type shrinkage, and that the additional shrinkage experienced during the more severe agitation of the fabric at a 1-lb. load was a felting type of shrinkage akin to that which occurs with wool. The difference between shrinkages at the two loads was then adopted as a measure of felting or progressive shrinkage.

Results and Discussion

The Effect of Yarn Twist and Twist Direction

One hundred fabric samples with similar construction, 60 ends by 40 picks, were woven on the same loom using warps and fillings made on the same system throughout. The warp and filling yarns were spun from 1½-den. 1 9/16-in. Bright Fibro into 20/1 yarns with twist multipliers ranging from 2.75 to 3.75 in steps of 0.25 twist multiplier. Ten warps were made and short lengths of all the fillings were woven across each warp, giving 100 fabrics covering combinations of amount and direction of twist (S and Z) in warp and filling from 2.75 to 3.75 twist multiplier.

The fabrics were desized in a solution of 1% Rhozyme and 1% Rapidaze at 180° F. for 30 min. using a liquor/cloth ratio of 150/1. Complete removal of size was checked with a starch indicator. They were subjected to 40 repeated launderings in a Frigidaire home-type washer with both 8- and 1-lb. dry washer loads, water temperature of 140° F., and 0.1% commercial soap (Lux).

The fabrics were dried on a flat bed press and dimensions measured after each tenth wash cycle.

The effect of increasing yarn twist upon both relaxation type and felting type shrinkage is shown in Figures 4 and 5. It appears that regardless of twist direction, increases in the amount of twist result in increases of both types of shrinkage. It is also ap-

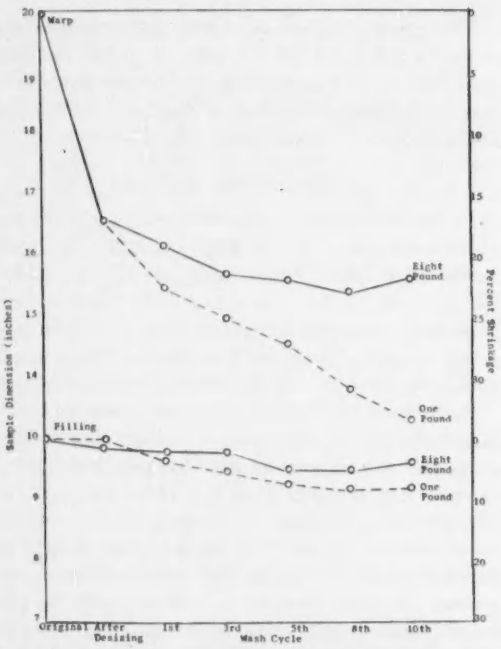


Fig. 3. A comparison of the laundering shrinkage curve of 1½-den. 1 9/16-in. Fibro (20/1, W+F, 60×40) at 8- and 1-lb. loads.

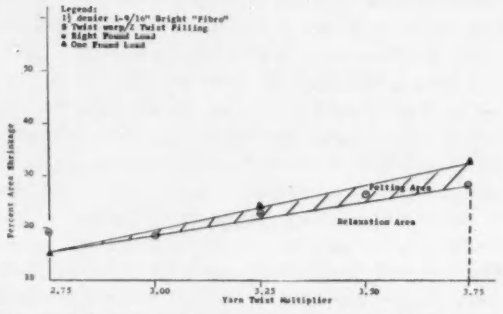


Fig. 4. The effect of yarn twist and twist direction upon viscose rayon staple fabric shrinkage after 40 launderings.

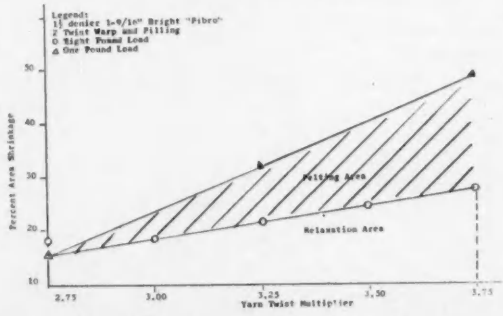


Fig. 5. The effect of yarn twist and twist direction upon viscose rayon staple fabric shrinkage after 40 launderings.

parent that, when the warp and filling yarns are of similar twist direction, felting type shrinkage is much more likely to occur.

Although none of the samples fulled more than to a slight extent with an 8-lb. load, there is a marked difference in the 1-lb. load samples, especially where the warp and filling twists are in the same direction. This additional effect is illustrated in Figures 6 and 7. It is apparent from this that greater fulling occurs when the fibers in the yarns at point of contact are approximately parallel to each other and that the degree of fulling is reduced when the fibers cross each other at approximately right angles.

In an attempt to find a more quantitative method of measuring the degree of apparent fulling and to check the soundness of our data, air permeability (Gurley) and fabric thickness (C & R Tester) measurements were made on the sample after 40 launderings. Reasonable correlation was found between subjective evaluation of fulling and the following fabric properties: area shrinkage, fabric thickness, air permeability, and bulk density. At the present state of knowledge, it appears that change in fabric thickness is probably as good a way as any of obtaining a quantitative measure of fulling.

The Effect of Fabric Properties

A series of fabrics with different fabric properties such as texture, yarn size, fiber denier, and staple length were woven to investigate the effect of these properties upon laundering shrinkage. Details of fabric constructions are given in Table II.

Evaluation of laundering shrinkage consisted of 10 repeated launderings in a Frigidaire automatic home washer using Tide detergent (0.1% concentration) at a water temperature of 140° F. Both 8- and 1-lb. dry washer loads were used to measure the two types of shrinkage.

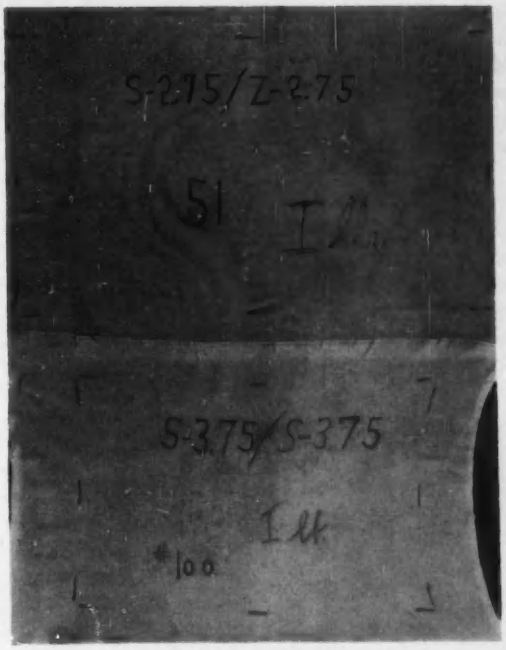


Fig. 6. The effect of twist and twist direction upon fabric shrinkage.

TABLE II. Fabric Details of Viscose Staple Samples Used in Determining Effect of Fabric Properties Upon Laundering Shrinkage

	Fabric construction	Cover* factor
1.	20/1 (60 × 58) Plain, 1½ × 1 9/16-in. Bright	26.2
2.	20/1 (60 × 52) Plain, 1½ × 1 9/16-in. Bright	24.8
3.	20/1 (60 × 40) Plain, 1½ × 1 9/16-in. Bright	22.1
4.	20/1 (60 × 34) Plain, 1½ × 1 9/16-in. Bright	20.8
5.	20/1 (68 × 50) Plain, 1½ × 1 9/16-in. Bright	26.2
6.	20/1 (52 × 52) Plain, 1½ × 1 9/16-in. Bright	23.2
7.	10/1 (44 × 36) Plain, 1½ × 1 9/16-in. Bright	25.3
8.	30/1 (74 × 61) Plain, 1½ × 1 9/16-in. Bright	24.6
9.	40/1 (84 × 74) Plain, 1½ × 1 9/16-in. Bright	24.9
10.	20/1 (60 × 41) 2 × 2 Basket, 1½ × 1 9/16-in. Bright	22.4
11.	20/1 (62 × 41) 2 × 1 Twill, 1½ × 1 9/16-in. Bright	23.0
12.	20/1 (61 × 41) Plain, 1½ × 1½-in. Bright	22.8
13.	20/1 (61 × 41) Plain, 3 × 1 9/16-in. Bright	22.8
14.	20/1 (60 × 41) Plain, 3 × 2-in. Bright	22.4

* $K = \frac{\text{ends/in.}}{\sqrt{N}} + \frac{\text{picks/in.}}{\sqrt{N}}$; N = cotton count of yarn.

The effect of texture. The effect of increasing cover factor upon the laundering shrinkage of viscose rayon staple fabric is shown in Figure 8. As can be seen from these results, cover factor has a different effect upon the two types of shrinkage. As with cotton fabrics, tight rayon fabrics washed with little agitation shrink more than looser fabrics, due to the increased effect of yarn swelling. On the other hand, as with wool fabrics, an increase in fabric cover factor or compactness results in a decrease in felting type shrinkage due to fiber movement. This felting type shrinkage becomes quite low as the jamming point is reached.

The effect of yarn size. An experiment was next designed to evaluate the effect of yarn size alone upon laundering shrinkage. Fabrics were woven from yarns of different count with the texture (ends and picks per inch) varied accordingly to give a constant cover factor of approximately 25.0. The yarns for these fabrics were spun from $1\frac{1}{2}$-den. $1\frac{9}{16}$-in. Fibro with the same twist multiplier (3.5) to eliminate, as far as possible, all variables except yarn count.

According to the two mechanisms of felting and swelling shrinkage, little effect of varying yarn number upon laundering shrinkage is to be expected if the fabric cover factor is held constant. The experimental results bear this out, as shown by Figure 9.

The effect of fiber denier and staple length. Previous experience in evaluating various viscose staples in regard to laundering shrinkage has shown that coarser denier fibers tend to make more stable fabrics than finer deniers. In order to determine the magnitude of the effect of both fiber denier and staple length upon both phases of laundering shrinkage (fiber swelling and felting), fabrics of similar texture, yarn twist, and count were woven from several viscose rayon staples which varied in denier and staple length.

Figure 10 illustrates the effect of fiber denier and staple length upon fabric laundering shrinkage. It is apparent that the effect of these variables on the fiber swelling type of shrinkage is quite small, as indicated by the 8-lb. load test. However, it is seen that both lower denier and longer staple length increase the felting type of shrinkage (1-lb. load)

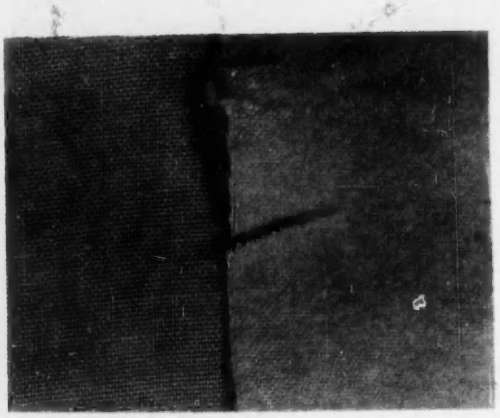


Fig. 7. The effect of twist and twist direction upon the fulling effect. Left, 3.75S/3.75S; right, 2.75S/2.75Z.

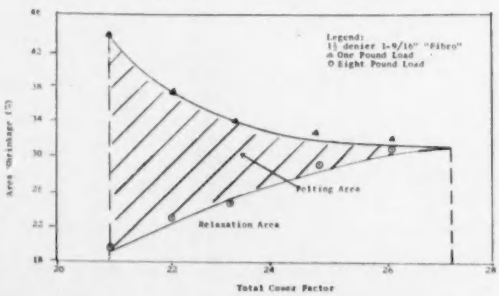
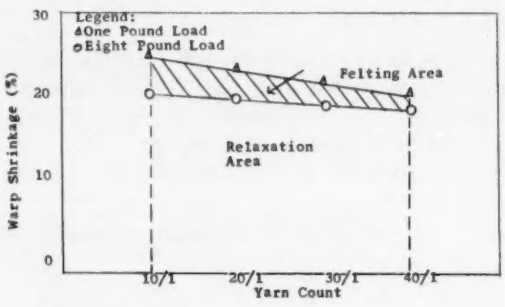


Fig. 8. The effect of fabric cover factor on fabric laundering shrinkage.



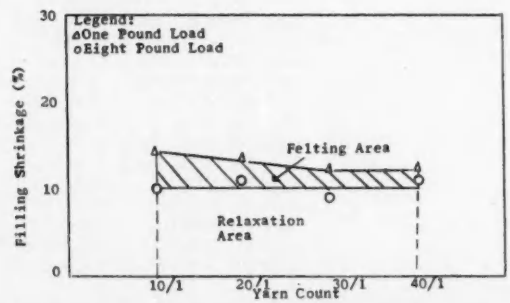


Fig. 9. The effect of yarn count at a constant fabric cover and twist multiplier (3.5) upon fabric laundering.

TABLE III. Single Fiber Properties of Various Cellulosic Staple Fibers

Fiber	Tenacity, g./den.		Elongation at break, %		Initial modulus, g./den.		Stress at 5% stretch, g./den.		Fiber water imbibition, %
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	
1. M-95 ($1\frac{3}{4} \times 1\frac{7}{16}$ in.)	3.21	2.62	26.3	31.7	27.0	3.8	0.79	0.19	68
2. Colvadur ($1-1\frac{3}{4} \times 1\frac{1}{2}$ in.)	3.56	2.34	23.4	23.9	39.7	3.8	1.03	0.22	89
3. Toramomen ($1\frac{1}{2} \times 1\frac{1}{2}$ in.)	3.06	2.72	8.2	12.0	51.7	8.4	1.86	0.77	59
4. D-35 ($1\frac{1}{2} \times 1\frac{9}{16}$ in.)	2.30	1.65	13.2	15.1	37.3	7.0	1.08	0.40	41
5. Fiber 109 ($1\frac{1}{2} \times 1\frac{1}{2}$ in.)	3.99	3.53	27.2	29.2	36.3	4.1	0.89	0.21	67
6. Fibro ($1\frac{1}{2} \times 1\frac{9}{16}$ in.)	2.32	1.47	24.8	26.8	32.8	3.4	0.76	0.19	110
7. M-95 (D-35)	2.90	2.57	16.7	19.5	—	—	—	0.62	46

markedly. This is in accordance with the results of Speakman [18] on wool.

Since the force to extend a given fiber a small amount varies with fiber denier and since ease of extensibility when wet is universally accepted as one of the properties which causes wool to felt, these facts suggest strongly that ease of extensibility in the wet state may be the fiber property which is most important in influencing the progressive shrinkage of fabrics.

The effect of weave type. It is generally recognized that weaves with longer floats and fewer interlacings are disturbed less by fiber and yarn swelling. This tends to improve stability to the swelling or relaxation type of shrinkage. In order to gain an idea of the magnitude of this effect upon viscose staple fabrics, a plain, 2×1 RH twill and a 2×2 basket weave were woven from similar yarns with the same texture for evaluation of laundering shrinkage.

In regards to swelling type shrinkage, weaves with fewer interlacings and less crimp should exhibit less shrinkage in accordance with Collins' theory. This effect was found in the 8-lb. load tests (Figure 11).

From the results obtained for the 1-lb. load tests (approximation to felting type shrinkage), it is apparent that the twill weave does not fall in line with previous trends. The twill weave appears to be peculiarly liable to felting shrinkage, and there is possible interaction between twill line and yarn twist direction.

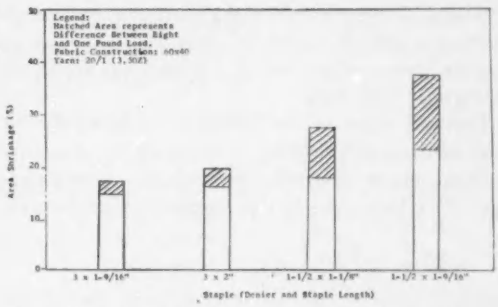


Fig. 10. The effect of viscose rayon denier and staple length upon fabric laundering shrinkage at constant yarn twist and fabric construction.

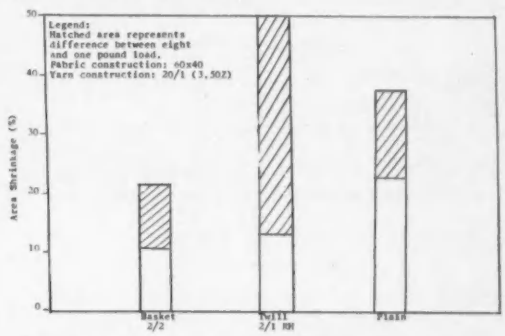


Fig. 11. The effect of weave type (constant texture) upon fabric laundering shrinkage.

The Effect of Fiber Properties

At this stage of the investigation, it was felt that sufficient knowledge of the effects of yarn and fabric properties had been obtained in order to evaluate intelligently the effect of fiber properties. A range of experimental fibers was available with different degrees of lateral molecular order, some wholly cellulosic, and some cross-linked to varying degrees. From these were chosen for investigation a group covering a range of degree of swelling and of tensile

properties, and fabrics of similar construction were woven from them. A fabric construction was chosen which would show both fiber swelling and felting shrinkage for rayon staple fabrics. Fiber swelling and felting shrinkage were determined as described earlier.

Load–extension curves on both dry and wet single fibers were obtained on a Table Model Instron tester using a 1-in. gauge length and a rate of extension of 60%/min. From these curves, tenacity, elongation at break, initial modulus, and stress at 5% stretch were calculated.

Degree of swelling was estimated by measuring the percent water imbibition of the fibers after wetting and extracting with an acceleration of 1000 G for 5 min.

The various cellulosic fibers used and their single fiber properties are given in Table III. Typical dry and wet stress–strain curves of these fibers are shown in Figures 14 and 15.

Previous work in the literature indicated the degree of diameter swelling of fibers to be associated with the degree of swelling or relaxation type shrinkage. Good correlation was found to exist between fiber water imbibition and shrinkage at an 8-lb. load (relaxation type), as shown in Figure 12.

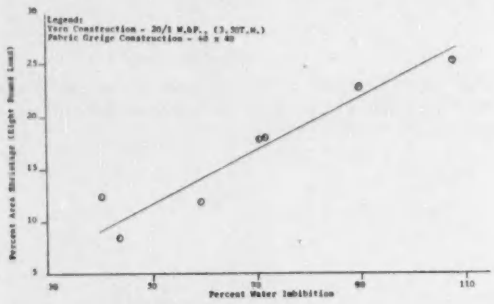

Legend:
Yarn Construction - 20/1 M.S.P., (3,207.M.)
Fabric Greige Construction - 48 x 48
Percent Area Shrinkage (Light Bound Load)
Percent Water Imbibition

Fig. 12. The effect of fiber swelling upon swelling type fabric shrinkage after desizing and 10 launderings.

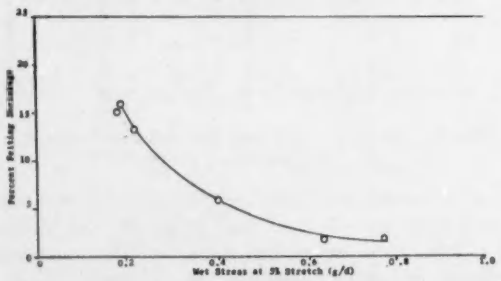


Fig. 13. The relationship between felting shrinkage after desizing and 10 launderings and ease of fiber extension when wet.

The relationship between ease of fiber extension when wet and felting type shrinkage is shown in Figure 13. These results indicate a clear and functional relationship between these two properties. Single fiber wet initial modulus was also found to exhibit good correlation with felting type shrinkage; stress at 5% extension is an approximate measure of the same fiber property. From these results, it appears that in order for cellulosic fibers to have adequate inherent resistance to laundering shrinkage they should have a wet stress at 5% extension of at least 0.6 g./den. or an initial wet modulus of at least 8 g./den.

It is also notable that Toramomen, a fiber which fibrillates very early and severely in the washing process, does not exhibit felting type shrinkage. This would indicate that degree or ease of fibrillation is not a measure of the felting potential of cellulosic fibers.

Summary and Conclusions

An investigation has been carried out on the fundamentals of laundering shrinkage of fabrics made from cellulosic fibers. The results of this investigation indicate the following.

Pure finished rayon staple fabrics when washed gently shrink because the fibers and yarns swell,

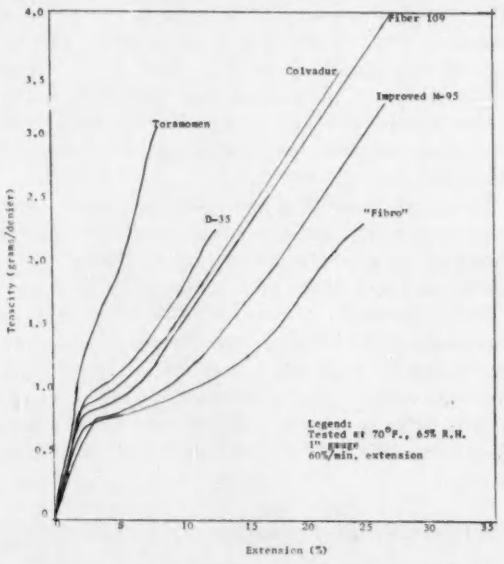


Fig. 14. Typical dry single fiber stress–strain curves.

causing a readjustment in crimp and consequent change in the dimensions of the fabric.

The same fabrics, when washed vigorously, undergo an additional "felting" type of shrinkage similar in most respects to that undergone by wool.

Fiber Swelling Type

The fiber swelling type of shrinkage is, as would be expected, dependent on the degree of swelling of the fibers in water.

This type of shrinkage may be reduced to a minimum by weaving more open cloths with fewer interlacings, or by weaving fabrics so tightly that when the fibers and yarns swell, they jam together and restrict shrinkage of the fabric.

Coarser deniers and shorter staples shrink a little less than finer deniers and longer staples, probably because of the slightly bulkier yarns obtained from coarse deniers and short staples.

Felting Type

Although the swelling type of shrinkage of rayon staple fabrics may be reduced by weaving open cloths with loose weaves, when these fabrics are washed vigorously, they felt and shrink to a very marked degree.

Cellulosic fibers which are harder to stretch when wet do not suffer from this grave disadvantage. Stress at 5% extension when wet has been found to be the best measure of the inherent felting shrinkage potential of cellulosic fibers. Fibers with a stress at 5% extension of less than about 0.3–0.4 g./den. are likely to felt to an embarrassing degree when washed vigorously.

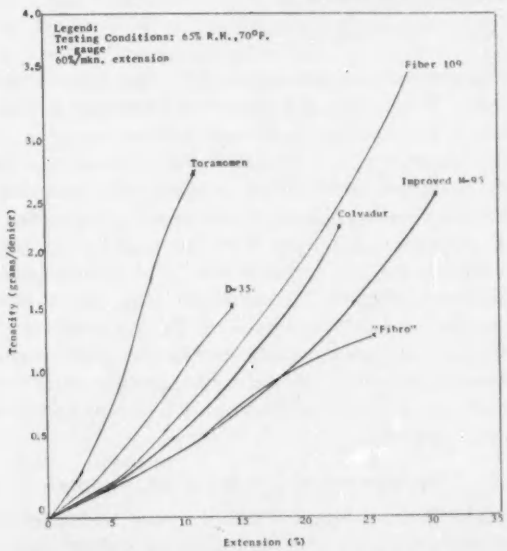


Fig. 15. Typical wet single fiber stress–strain curves.

The felting shrinkage of fabrics made from rayon staple is highly dependent on:

1. Yarn twist: Higher twists give more shrinkage.
2. Twist direction: There is less felting shrinkage when warp and filling twist directions are opposed.
3. Denier: Coarser deniers felt less.
4. Staple length: Longer staples felt more.
5. Fabric construction: Looser fabrics felt more.
6. Weave: Twill weaves appear to be particularly liable to felt heavily.

The felting potential of different types of cellulosic fibers does not appear to be related to the degree of fibrillation in washing.

Relaxation of Fiber Stresses

Since this investigation was carried out on loom state fabrics desized in a relaxed manner, only the effects of fiber strains during processes up to and including weaving have been investigated.

The major source of fiber strains is likely to be in the wet finishing processes, and it appears likely that an increase in fiber stress at 5% extension will reduce shrinkage due to this probable effect. However, this point has not been investigated.

Acknowledgments

Appreciation is expressed to Mr. D. W. Broadwell and Mr. H. N. Gurley for the processing and weaving of all fabrics, to Mr. C. D. Dickey and Miss Billie Fussell for evaluation of laundering shrinkage, and to Miss Joe Jane Williams for determination of single fiber properties.

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Factors Affecting the Drying of Apparel Fabrics

Part III: Finishing Agents

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Abstract

The hanging strip water gradient determination and its interpretation on the basis of a capillary bundle model have been applied to a study of the effect of finishing agents on the water-holding capacity of cotton printcloth. Water repellents, cross-linking reactive resins, and surface resins all reduce the water capacity to varying degrees and thereby should make them easier to dry. However, the effect of water repellents is negligible if the fabric is wet out with a surface active agent or by mechanical action, both of which are normally met with in laundering. The reductions in capacity produced by reactive or surface resins are not affected by these factors.

EARLIER papers in this series have discussed the drying behavior of apparel fabrics under drip-dry conditions [3] and the characterization of the water-holding capacity of fabrics using a capillary bundle model [4]. The time required for drying fabric under these conditions is proportional to the amount of water held. The water-holding capacity can be considered to be made up of the volume of a bundle of continuous capillaries of various radii, the volume of a noncontinuous capillary system, and the sorptive capacity of the fibers themselves. The present paper deals with the application of this model to various fiber–liquid systems and particularly with the effect of finishing agents on the water-holding capacity of cotton printcloth.

Liquid concentration gradients were determined as described earlier [4] by hanging a wet strip of fabric in a closed chamber at 20° C. and, after equilibration, cutting it into sections whose liquid contents were determined gravimetrically. The fabric strips were 110 cm. long and were cut into 15-cm. sections after 2 cm. was discarded from the bottom.

Four groups of experiments were carried out. In the first, the water-holding capacities of three cotton fabrics were analyzed. In the second, the capacity of cotton printcloth to hold deionized water was compared with its retention of alcohol, aqueous alcohol, and Triton X-100 solution. The effects of a number of finishing agents on the water retention of printcloth were investigated in the third group. Finally, the effect on the water gradient curve of wetting the sample by thorough mechanical agitation was examined.

Comparison of Three Cotton Fabrics

The water concentration gradients in strips of cotton printcloth, sheeting, and lawn were determined after allowing 8, 24, and 48 hr. for equilibra-

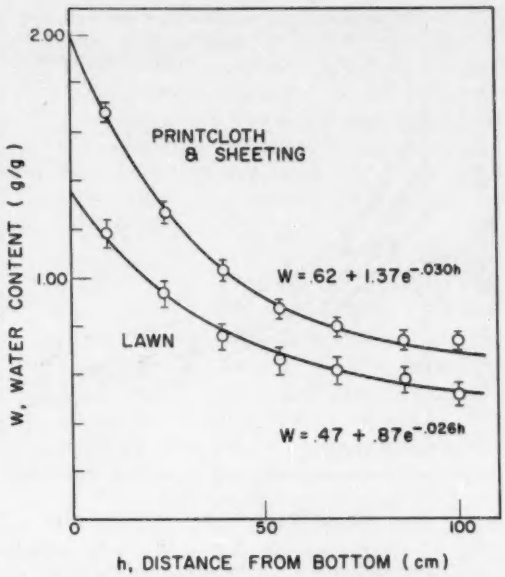

Fig. 1. Water concentration gradients in wet vertical strips of three cotton fabrics.

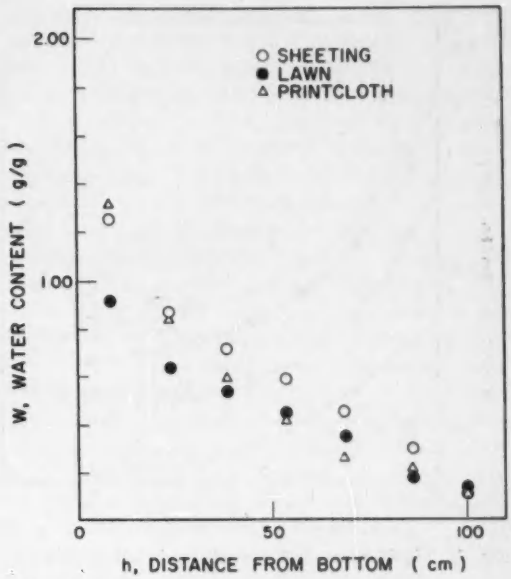

Fig. 2. Water concentration gradients in cotton fabrics resulting from capillary rise.

tion. The construction of these fabrics was given in Table I of the first paper in this series [3].

The data were subjected to an analysis of variance which indicated that there were no differences due to the three equilibration times nor between the printcloth and sheeting. The lawn, however, was different from the other two fabrics. There was also a time–fabric interaction which was shown to be due to the lawn. The 1% probability level was used in tests of significance. The data are plotted in Figure 1, using the averages over the three times and for the similar pair of fabrics. These data were fitted with the empirical equation used in developing the capillary bundle model [4], which has the form

$$W_h = a + be^{-kh}$$

where W_h is the water content at height h, a is the water held within the fibers and in noncontinuous capillaries, b is the maximum capacity of the continuous capillaries, and k is a constant which depends on the fabric. The equations obtained are on the figure and the curves shown were calculated from these equations.

An experiment similar to the above was carried out starting with dry fabric strips and letting their ends dip into water at the bottom of the chamber. The level of water was adjustable so that water depletion and length changes in the strip could be compensated for. Comparison of the data for 8, 24, and 48 hr. indicated that the rate of wicking was very slow in the 24–48 hr. interval, and that the 48-hr. data might be reasonably close to equilibrium approached from the dry side. These data are plotted in Figure 2 but could not be satisfactorily fitted with the equation.

Alcohol and Triton X-100 Solution

Gradient curves in printcloth after 24 hr. equilibration from the wet side were obtained for 0.01% aqueous Triton X-100 solution, 2B-ethanol, and a 50% (vol./vol.) solution of 2B-ethanol in water. The results are plotted in Figure 3; the constants of the fitted equations are given below.

	k	a, g./g.	b, g./g.
2B-ethanol	.030	0	.83
ethanol/water	.029	.22	1.24
0.01% Triton X-100	.033	.53	1.19

Effect of Finishing Agents

The effects of representatives of three classes of finishing agents on the water held by printcloth were investigated—water repellents, reactive resin precondensates, and surface resins.

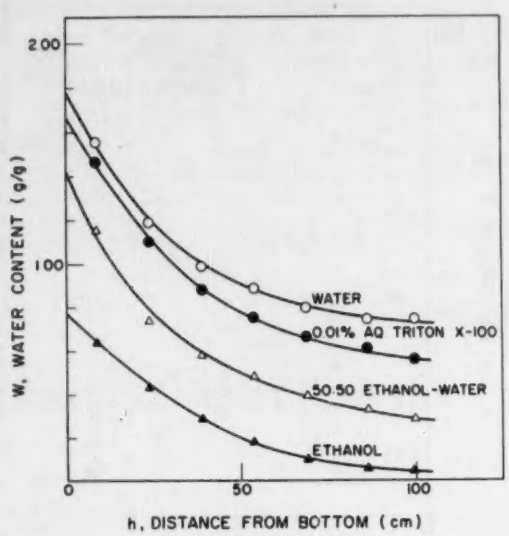

Fig. 3. Liquid concentration gradients in cotton printcloth.

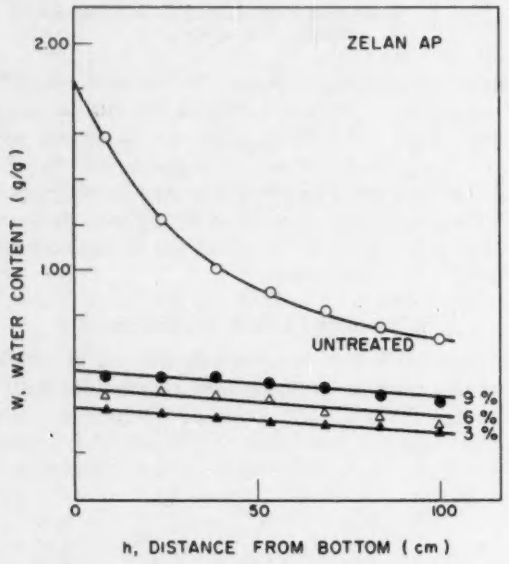

Fig. 4. Water concentration gradients in water repellent cotton printcloth.

Water Repellents

Samples of printcloth were treated with 3.6 and 9% solutions of Zelan AP Paste.[1] The solutions contained sodium acetate as a buffer and were applied on a laboratory padder which gave 80% wet pick-up.

[1] Du Pont trademark.

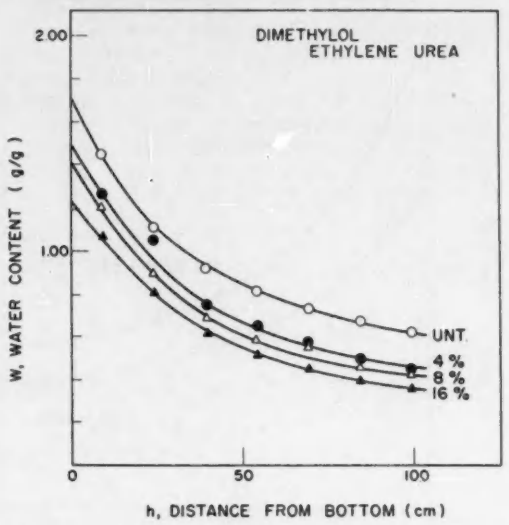

Fig. 5. Water concentration gradients in printcloth treated with various levels of dimethylol ethyleneurea (concentrations are percent solids fixed on the fabric).

The impregnated fabric was immediately cured for 10 min. at 150° C. Water gradient curves were obtained as described above using 24 hr. equilibration. The results are shown in Figure 4. An analysis of variance indicated that the negative slope of the curves was significant at the 1% level. The order of the treatment concentrations was unexpected but was confirmed in check experiments.

A 3% solution of paraffin wax in benzene was applied to printcloth and air-dried. The water concentration gradient of the fabric was determined after 2.5 hr. equilibration. The results were more erratic than usual due to difficulty in evenly wetting the sample, which was rather more water repellent than the Zelan treated fabrics. However, the average water concentration was lower than for Zelan, even though a short equilibration time was used. The average water concentration in the wax treated fabric was 0.407 ± 0.177 g./g., and there was no trend with height in the fabric. For the Zelan treatments the averages were 0.677, 0.809, and 0.993 ± 0.024 g./g. for the 3, 6, and 9% applications respectively. The limits indicated are ± two standard deviations.

Reactive Resin Precondensate

As an example of a reactive resin precondensate, dimethylol ethylene urea was applied to printcloth at levels of 5, 10, and 20%, using 0.2 mmol of NH_4Cl

per gram of precondensate as a catalyst. The applications were made on the lab pad, and the samples were dried at room temperature, cured for 10 min. at 150° C., and given a light scour to remove soluble residues. Water concentration gradient determinations were carried out allowing 24 hr. for equilibration, and the fabrics were analyzed for fixed resin by the acid extraction procedure. The results are plotted in Figure 5.

Surface Resin

Printcloth samples were treated with dispersions containing 5, 10, and 15% solids of a soft acrylate emulsion polymer, Rhoplex S-1.[2] The dispersions were applied at 80% wet pick-up, and the impregnated samples were dried at 150° C. Water gradient data were obtained after 2.5 hr. equilibration and are shown in Figure 6. The curves for untreated fabric in Figures 4, 5, and 6 represent controls run with each of the experiments, which were carried out at about 6-month intervals. The untreated curve in Figure 4 is different from that in Figure 5, but is very close to that in Figure 6. The first two were run with 24 hr. equilibration time and the last with only 2.5 hr. The three curves must be regarded as equivalent within experimental error.

Effect of Mechanical Action

Ordinarily, drying of apparel fabric takes place after the fabric has been wet out by some procedure which involves mechanical action, such as laundering. It might be expected that changes in water-holding capacity produced by surface effects would be less pronounced if measured after being wetted in this way. The effect of such wetting on the changes in capacity produced by various finishes is demonstrated by the following experiment.

Cotton printcloth samples were treated by the procedures described above with (1) 20% dimethylol ethylene urea, (2) 15% solids Rhoplex S-1, (3) 15% solids Rhoplex AC-33, (4) 3% Zelan AP Paste, and (5) water. Water gradient curves were determined in the usual manner, wetting the sample by pouring water on from the top, and also by shaking the strip in water for 15 min. on a mechanical shaker before hanging it in the test chamber. Samples from each of these treatments were also run using 0.01% Triton X-100 solution instead of deionized water, the wetting being done by pouring. The water repellent sample was also tested with both mechanical agitation and the wetting agent. In all cases, 24 hr. was allowed for equilibration. Duplicate runs were made and the results were averaged.

The results are given in detail in Table I along with summaries of the analyses of variance which were carried out. No interactions were significant in the analyses shown. The data from the two surface resins were grouped together and neither the resin type nor wetting procedure gave rise to significant differences. In the case of dimethylol ethylene urea treatment the wetting procedure main effect is significant due to the lower amount of water held in the presence of the wetting agent. The wetting main effect is significant with the water repellent treatment also, but in this case is due to a higher water retention in the presence of X-100. There is of course a large difference between the concentration level obtained by pouring water on the Zelan treated fabric and that obtained by using mechanical action, a wetting agent, or both. In the analysis of variance only the latter three were compared. The wetting main effect was not significant with the untreated fabric. In all the tests of significance the 1% probability level was used.

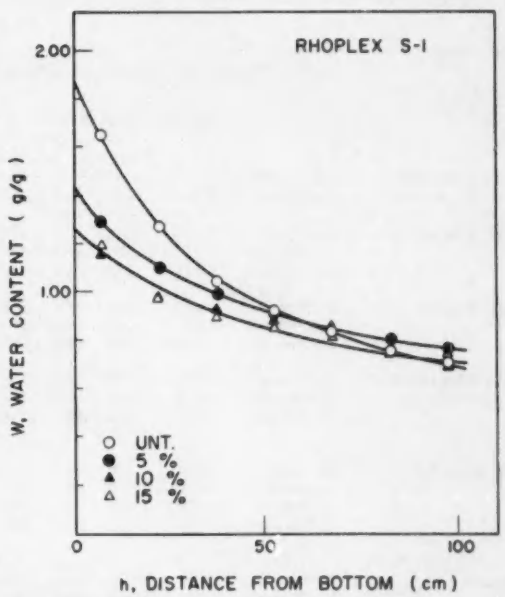

Fig. 6. Water concentration gradients in cotton printcloth treated with surface resin (concentrations are percent solids applied to fabrics).

[2] Rohm and Haas trademark.

Discussion

The water gradient curves of Figure 1 give values of total water-holding capacity which are a little higher than those obtained from the rate of drying experiments [3]. The two sets of data are shown below.

	Water-holding capacity, g./g.	
	From water gradient	From drying experiments
Lawn	1.34	1.24
Printcloth	1.99	1.64
Sheeting	1.99	1.58

Earlier [3], it was pointed out that the water-holding capacities of these fabrics fit reasonably well the relationship between thickness and capacity observed by Fourt [1]. It should, however, be noted that among these three fabrics the capacity seems to be correlated more closely with the weight than with the thickness.

Since the time permitted for equilibration was not a significant factor in the first experiment described, it would appear that the 24-hr. period usually used is sufficient for a fairly close approach to the wet-side equilibrium. The latter is quite a bit higher than the values which can be reached in comparable times from the dry side, as shown in Figure 2. This is similar to the difference observed by Voyutsky and Peregudova [5], whose data were plotted by Steele [4]. In equilibration from the dry side, the non-continuous capillary system would be filled with difficulty, if at all, by diffusion through the fibers or by vapor transport and condensation. In general, it would appear to be more realistic to apply the model being used here only to measurements obtained by approach from the wet side so that equilibrium may be more nearly assured.

The capillary bundle model [4] predicts that the number of capillaries filled and the radius of the most frequently occurring capillary size will be dependent on the surface tension (γ) and the density (ρ_1) of the liquid used and on its contact angle (θ) with cellulose. The most frequently occurring (modal) radius is given by

$$r_{mod} = (k\gamma \cos\theta)/2\rho_1 g$$

The total area of the continuous system is given by

$$A = (b\rho_2)/2$$

where ρ_2 is the density of the fabric in grams per square centimeter. Table II gives the parameters of these equations for printcloth wet with various liquids as obtained from the data plotted in Figure 3. Ethanol and the ethanol–water mixture are held in

TABLE I. Water Concentration Gradients in Treated Printcloth

Treatment (% solids)	Wetting procedure	Water concentration gradients: Water conc. at various heights, g./g. 7.5 cm.	22.5	37.5	52.5	67.5	82.5	97.5	Analyses of variance*: Source of variance: Wetting procedure	Height	Residual	Total
15% Rhoplex S-1	H_2O pour	1.153	.844	.734	.623	.563	.524	.489				
	X-100 pour	1.126	.801	.683	.620	.584	.530	.496				
	H_2O mech.	1.215	.845	.726	.642	.594	.551	.472	SS .02697	.82476	1.01411†	1.86583
									df 5	6	30	41
15% Rhoplex AC-33	H_2O pour	1.076	.785	.669	.588	.544	.517	.478	MS .00539	.13746	.03380	
	X-100 pour	1.051	.769	.640	.580	.535	.503	.470		**		
	H_2O mech.	1.195	.845	.698	.613	.584	.543	.504				
20% Dimethylol ethyleneurea	H_2O pour	1.124	.751	.614	.536	.487	.434	.398	SS .01329	1.02579	.00676	1.04585
	X-100 pour	.972	.708	.580	.503	.445	.396	.355	df 2	6	12	20
	H_2O mech.	1.106	.766	.618	.534	.480	.432	.384	MS .00665	.17010	.00056	
									**	**		
3% Zelan AP	H_2O pour	.397	.349	.313	.286	.343	.324	.341				
	X-100 pour	1.535	1.070	.835	.721	.636	.588	.526	SS .02557	2.17920	.01579	2.22056
	H_2O mech.	1.428	1.076	.775	.600	.537	.580	.462	df 2	6	12	20
	X-100 mech.	1.557	1.034	.822	.725	.676	.627	.582	MS .01278	.36320	.00132	
									**	**		
Control	H_2O pour	1.536	1.122	.929	.838	.747	.686	.636	SS .00907	2.04043	.02220	2.07170
	X-100 pour	1.527	1.062	.883	.780	.725	.673	.620	df 2	6	12	20
	H_2O mech.	1.722	1.145	.898	.801	.746	.684	.626	MS .00454	.34007	.00185	
										**		

* Two stars indicate significance at 1% probability level.
† Nonsignificant resin effect pooled in residual.

considerably smaller amounts than water itself. The biggest change is in the water in the noncontinuous capillary system, which is shown in Figure 7. The average capillary size is much smaller with alcohol and the alcohol–water solution.

The changes in capacity effected by the various finishing treatments are summarized by the data in Table III, which are calculated from the results in Table I. The two Rhoplexes were indistinguishable in their behavior with all three wetting procedures, so the results have been averaged. Brackets in the second column indicate where wetting procedures were not significantly different.

Treatment of cotton fabric with a water repellent, such as Zelan or paraffin, reduces the capacity of both the continuous and noncontinuous capillary systems. The continuous system is, in fact, almost eliminated, as shown by the low slope of the lines for treated fabrics in Figure 4. These curves are not precise enough to be used to characterize the small remaining continuous capacity. This reduction in capacity resulting from the higher contact angle between water and the treated cloth can be overcome completely either by mechanical agitation of the fabric in water or by addition of wetting agent to the water. Since both of these factors are involved in even the simplest laundering procedure, it is obvious that water repellent treatments will not be particularly effective in reducing the drying time of cotton apparel after it is washed.

The changes produced by dimethylol ethylene urea, though smaller than those of water repellents, are more permanent. Both the continuous and noncontinuous capillary systems are reduced as much as 20–30% in capacity, while the average capillary size is somewhat increased. This can be seen in Figure 5 and Table III. The same results are ob-

TABLE II. Capacity of Printcloth for Holding Various Liquids

Parameter	Water	Ethanol	Water–ethanol	0.01% aq. Triton X-100
ρ_l, g./cm.³	1.00	0.79	0.91	1.00
γ, dynes/cm.	72.8	2.15	27.5	31.0
r_{mod}, microns	11.7	4.3	4.4	5.2
A, cm.²/linear cm.	.0089	.0066	.0099	.0095

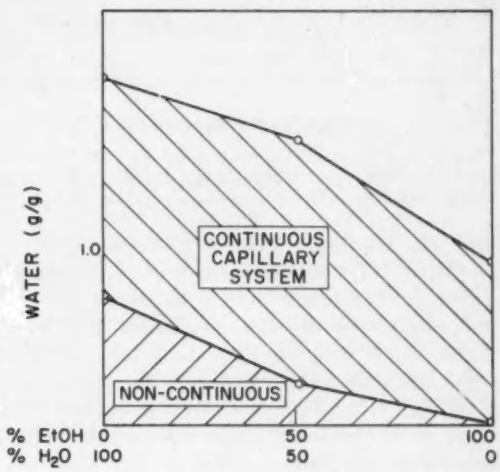

Fig. 7. Capacity of cotton printcloth for holding alcohol and water.

TABLE III. Water Capacity of Printcloth with Various Finishes

$W_h = a + be^{-kh}$

Treatment	Wetting procedure	a, g./g.	b, g./g.	k	r_{mod}, μ	A, cm.²/cm.
None	H_2O pour, X-100 pour, H_2O mech.	.52	1.16	.0243	9.0	.0093
Zelan AP	H_2O pour	.35	0	—	—	—
	H_2O mech.	.42	1.34	.0362	13.1	.0107
	X-100 pour	.60	1.31	.0458	17.0	.0105
Rhonite R-1	H_2O pour, H_2O mech.	.37	.93	.0330	12.3	.0074
	X-100 pour	.33	.81	.0304	11.3	.0065
Rhoplexes	H_2O pour, H_2O mech., X-100 pour	.48	.83	.0349	13.0	.0066

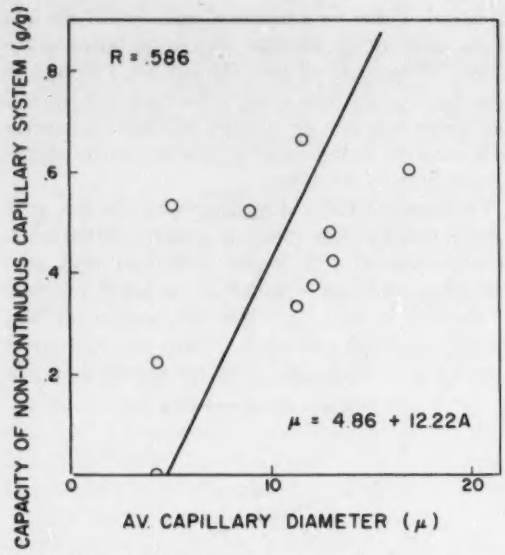

Fig. 8. Correlation of water-holding capacity of noncontinuous capillary system with average capillary diameter.

tained by either pouring water on the test strip or agitating it in the water mechanically. Pouring on a dilute X-100 solution gives a statistically different result which shows the same qualitative changes.

These results with water repellents and aminoplast resins confirm those of Lippert [2], who showed that the drying time of a cotton fabric was reduced from 42 min. to 33 min. by an unspecified resin treatment. The addition of a water repellent to his resin formulation did not change the drying time.

Acrylate emulsions also reduce the water capacity, probably only in the continuous capillary systems. The average capillary size is increased. The method of wetting made no difference in the results, and the harder, tougher resin Rhoplex AC-33 gave the same effect as Rhoplex S-1.

It can be concluded from these results that when reactant resins and surface resins are used in wash-wear finishes for cotton, both classes of materials may be expected to contribute to reduced water-holding capacity in the fabric, thereby shortening the time required to dry it. *A priori*, one would expect that these two classes of resins would act through different mechanisms so that their effects would be at least partly additive.

All of these agents seem to increase the modal average of the capillary size distribution. The meaning of this is not clear. If one also considers the results obtained with ethanol, there is a strong indication that the average radius is related to a, the capacity of the noncontinuous capillary system. These quantities are plotted against each other in Figure 8. The correlation coefficient is 0.586, which is significant at the 5% level. Since the capillary size is calculated from b, the continuous system capacity, it might be expected that there would be a correlation between these quantities. However, in this case the correlation coefficient is -0.220 and is far from significant.

Conclusion

Since finishes cannot change environmental factors involved in the drying of apparel fabrics, they can affect the drying time only by changing the amount of water held by the wet fabric. Water repellents, reactive cross-linking resins, and surface polymers all reduce the water-holding capacity of fabric to various degrees. However, water repellents show no effect if mechanical agitation or a surface active agent is used in wetting the fabric. The 20–30% reductions in capacity due to reactive and surface resins are not affected by either of these factors.

The capacity of fabric for holding alcohol or alcohol–water mixtures is lower than for water alone. The major part of the difference is attributed to that portion of the liquid which acts as if it were in a noncontinuous capillary system.

Note

The following corrections should be made in Part II [TEXTILE RESEARCH JOURNAL **28**, 144–147 (1958)].

1. The symbol ν should be replaced with the conventional symbol for surface tension γ.

2. Page 147, column 1, line 10. The first letter in the parentheses should be k instead of b.

3. Page 147, column 1, line 17. The word "fiber" should be "fabric."

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The Change in Stress on Wetting and Drying Wool Fibers

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Abstract

When a wet wool fiber is strained to a fixed extension, allowed to remain at this extension for a time, and then dried, the stress in the fiber rises. This rise of stress is independent of the time as long as it is greater than about 1 min. and is also independent of a number of chemical and physical modifications to various fibers. The rise in stress is dependent on the strain and increases to a maximum value at about 30% strain. Between 30% and 50% strain no further increase was recorded. From the evidence presented, it is suggested that drying the fiber in a strained state introduces strained hydrogen bonds, which are responsible for the stress rise on drying.

Introduction

If a single wool fiber is held strained in water at room temperature, the stress rapidly falls in the fiber and reaches a relatively steady value in about 60 min. [9]. In this time the stress in the fiber has fallen by about 33%. If the fiber, still strained, is conditioned to 0% relative humidity, on release nearly all the strain in the fiber remains. This property of wool is known as cohesive set and has been described many times in the literature [7, 13]. It is the basis of cold water setting of waves in human hair.

As part of a research program on cohesive set, the author has observed the stress in a strained fiber in water at 20° C. and then at 0% relative humidity. Since it is the stress in the dried fiber which causes the small decrease in the strain when the set fiber is released in the dry state, it was felt that a knowledge of the variation of this stress with differing conditions of time of drying of the fiber and with differing chemical and physical modifications would increase our understanding of the process of cohesive set.

Experimental Technique

A schematic representation of the experimental set-up is shown in Figure 1.

The fiber (F) was in the form of a loop with both ends held by a tapered plug (P) in a holder (H). The loop passes over a hook connected to a force-sensitive transducer, a resistance bridge type manufactured by Statham Instruments. The output of this bridge (which is balanced at zero force) is fed into a potentiometric recorder. The transducer is kept fixed and the plug holder is attached to a screw thread (S), which could be driven by hand or at a constant rate by a controlled motor. Where the initial force was of no consequence, the fiber was extended by rotating the screw thread by hand. When a consistent starting point for stress relaxation of the fiber under test was required the fiber was extended at a fixed rate. All the experiments

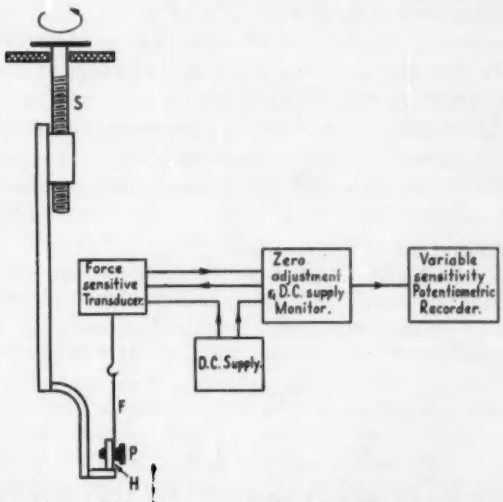

Fig. 1. A schematic representation of the apparatus used to measure the force at a fixed extension in a fiber loop.

were carried out at 20° C. in water, or in Analar glycerol when a dry state was required. It was shown that at room temperature the same results were obtained with the fiber either in Analar glycerol or in air which was dried by blowing over concentrated sulfuric acid. For convenience the former technique was preferred.

Except where the variation of some parameter against strain was being measured, the strain at which all the measurements were made was 20%. The wool fibers used were from penned Corriedale sheep, hand fed for uniformity of growth and supplied by the Sheep Biology Laboratory of the C.S.I.R.O. These fibers have a coefficient of variation of cross-sectional area along their individual lengths of 5%.

Experiments and Results

The force-time curves for single wool fibers at a number of fixed strains in water at 20° C. were determined. After a definite time t, at which the force in the fiber was F_t (see Figure 2), the fiber, at the fixed strain, was suddenly dried by plunging it into Analar glycerol. The force in the fiber rose rapidly, and after 30 min. was accepted as being steady at a value of F_D. The experiment was repeated on each fiber a number of times, varying the value of the time t at which the drying of the fiber was commenced. This type of measurement is similar to the one carried out by Algie [2] on horse hair. Between each experimental test the fibers were relaxed in water at 53 ± 1° C. for 1 hr. in order to return the fibers to their original mechanical state. It was found that at a fixed strain, although F_t varied with time, the value of $(F_D - F_t)$ remained constant within the resolution of the apparatus for t greater than about 1 min. Typical results for four different fibers at four different strains are shown in Table I. The remarkable stability of the value of $(F_D - F_t)$ is shown in Fiber 4 of Table I, where over the range 40–8,220 min. the value of F_t changes by almost 50% and $(F_D - F_t)$ is within the limits 25.5 ± 0.5.

The relationship at t = 30 min. between $(F_D - F_t)$ and strain was then determined for each of a number of fibers. A typical curve of strain versus $(F_D - F_t)$ is shown in Figure 3. The value of $(F_D - F_t)$ increases with strain up to strains of about 30%, beyond which the value shows little increase up to the maximum strain investigated (50%). At a strain of 20% the value $(F_D - F_t)$ is 0.9 of the maximum value. This strain of 20% is in the yield region of the load extension curve of keratin fibers, and the mechanical properties at this strain level are recoverable by relaxation. For this reason 20% strain was chosen as the standard value at which $(F_D - F_t)$ was measured for a large number of both normal and physically and chemically modified fibers.

$(F_D - F_t)$ was measured for 11 unmodified

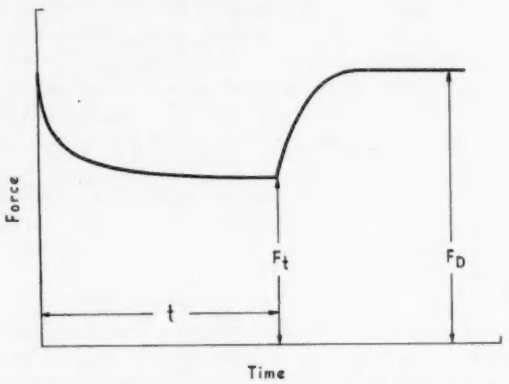

Fig. 2. A diagram representing the variation with time of force in a wet fiber at a fixed strain up to a time t, when the force in the fiber drops to F_t. At time t the atmosphere around the fiber was changed to Analar glycerol or dry air. The force in the dry fiber reached an equilibrium value of F_D.

TABLE I. The Increase of Force in a Fiber $(F_D - F_t)$ on Being Dried at Time t after Stress-Relaxing in Water at Various Strains; F_t and $(F_D - F_t)$ in Arbitrary Units

Fiber 1: 20% strain			Fiber 2: 25% strain			Fiber 3: 30% strain			Fiber 4: 40% strain		
t, min.	F_t	$(F_D - F_t)$	t, min.	F_t	$(F_D - F_t)$	t, min.	F_t	$(F_D - F_t)$	t, min.	F_t	$(F_D - F_t)$
~ 0.05	61	29.6	0.2	55.5	29.0	1.8	33.7	24.5	40	40.8	25.2
~ 0.1	58	31.5	0.3	53.2	28.5	140	29.3	24.5	1,052	32.4	26.0
0.2	57.5	32.5	2.5	49.5	29.6	1,320	25.8	25.2	2,580	29.0	25.9
12	48.6	34.0	17.5	45.6	31.2				3,930	26.1	25.0
48	46.8	35.2	47.5	44.7	30.8				8,220	23.6	25.5

fibers and reduced to a stress for purposes of comparison. The value of this stress averaged for the fibers was $1.8_5 \times 10^8$ dynes/cm.^{2} The distribution of stress values for the individual fibers had a coefficient of variation of 11%. The value of F_t at $t = 60$ min. was also measured for these fibers at 20% strain in water (see Table II). At this time level, although stress relaxation had not completely ceased, the value of the force was steady and useful as a comparison with the chemically and physically modified fibers that were also tested.

Measurements of $(F_D - F_t)$ and F_t at $t = 60$ min. (called F_{60} in Table II) and 20% strain were carried out for a series of fibers which had undergone the following physical or chemical treatments.

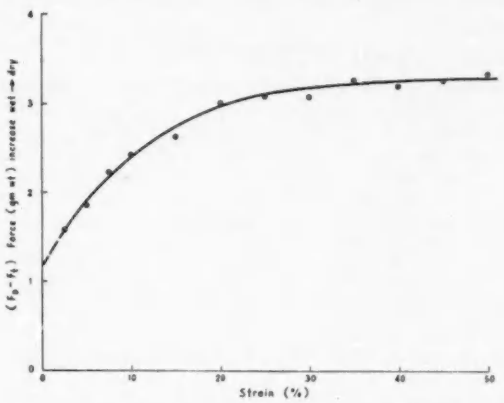

Fig. 3. The variation of the force $(F_D - F_t)$ in a fiber at various strains. The fiber illustrated had a wet diameter of 46 μ.

TABLE II *

Treatment	F_{60}/A, dynes/cm.^{2}	$(F_D - F_t)/A$, dynes/cm.^{2}
Normal	$2.6_8 \times 10^8$	$1.8_5 \times 10^8$
Thioglycollic acid pH 5 (21 hr.)	0.6×10^8	$1.9_8 \times 10^8$
Iodinated	1.7×10^8	$1.6_7 \times 10^8$
Van Slyke	2.2×10^8	$1.7_3 \times 10^8$
Ultraviolet irradiated	1.6×10^8	$1.9_4 \times 10^8$
Hexamethylene tetramine	2.3×10^8	$1.7_2 \times 10^8$

* The force F_{60} was measured at a strain of 20% in water after 60 min. for Corriedale wool fibers, after various physical and chemical treatments as indicated. $(F_D - F_t)$ is the rise of force in each of these fiber treatments when the fiber is dried after having been strained for a period at 20% extension. For purposes of comparison the forces have been reduced to stresses by dividing by the cross-sectional area A of the fiber being tested. This value A is for the wool fiber in water unstrained.

1. Treated in Van Slyke reagent (34 ml. of water, 8.69 g. of $NaNO_2$, and 7.2 ml. of glacial acetic acid at 20° C. for 27 hr.). This treatment causes nitrosation of the tyrosine residues [12].

2. Iodinated by the technique described by Richards and Speakman [8]. This treatment converts tyrosine to di-iodotyrosine.

3. Treated in 1 N thioglycollic acid at pH 5 for 21 hr. at 37° C. This treatment according to Swan [10] reduces about 50% of the cystine sulfide links in the wool structure.

4. Normal fibers irradiated at 15 cm. from a 125 W high pressure mercury-in-quartz lamp for 15 min.

5. Fibers treated [6] in 1% hexamethylene tetramine in acidic solution for 45 min. at 90° C.

As Table II shows, values of F_{60}/A (where A is the cross-sectional area of the wet fiber) were treatment-dependent and lay within the range 0.6×10^8 dynes/cm.^{2} to $2.6_8 \times 10^8$ dynes/cm.^{2}; i.e., the values differ by as much as a factor of 4.5. However, the values of $(F_D - F_t)/A$ are confined to a very narrow range between 1.67×10^8 and $1.9_8 \times 10^8$ dynes/cm.^{2} In fact, considering the variation indicated earlier for a normal unmodified fiber, the value of $(F_D - F_t)/A$ appears to be invariant to the chemical or physical modifications applied. For none of the treatments listed in Table II does the value differ by more than 10% from the value for a normal fiber, i.e., $1.8_5 \times 10^8$ dynes/cm.^{2}

Discussion

When a wool fiber is extended to a fixed strain in water and then dried, the increase in stress on drying is independent of time at which drying was commenced for times greater than the order of a minute.

The slightly lower values obtained for shorter times may be due to the fact that during straining the equilibrium regain of the fiber increases, which means that the fiber in the first minute or so after straining has not reached moisture equilibrium with its surroundings. That the wool fiber becomes more accessible to water during straining is implied in the results on deuterium–hydrogen exchange in fibers during straining [3] and in the results on electrical conductivity of strained fibers [1, 4]. Further, Treloar has shown an increase in water uptake of horse hair with strain. Preliminary ex-

periments have been carried out in this laboratory on fibers initially equilibrated unstretched in water. These fibers were rapidly transferred into silicone oil and stretched to 10 and 20%. The behavior on stress relaxation of these fibers indicates that they are equivalent to the same fiber in an atmosphere well below 100% RH. The simple interpretation of these results is that the regain, for equilibrium with 100% RH at these strains, is higher than that for the unstrained state, so that on being stretched these fibers act as if at a lowered relative humidity, since no water is available from the surroundings.

The stress increase in the extended fiber on drying is nearly independent of quite a range of chemical and physical modifications, despite the wide range of stress values in wet, strained fibers produced by these modifications. The stress increases as a result of water removal, indicating that loss of water allows the formation of bonds opposing the strain on the fiber. These bonds would have to be unaffected by the modifications to the fibers. It seems reasonable to conclude that a hydrogen bond mechanism is involved.

It is worth noting that on release in the dry state, after being held strained at 20% extension for 1 hr., the unmodified wool fibers contracted 2–3%. This means that the strained bonds introduced by the removal of water from the fiber structure have an effective Young's Modulus $\approx 1.85 \times 10^8/0.025$ dynes/cm.^{2}, i.e., about $0.7_4 \times 10^{10}$ dynes/cm.^{2}, taking 2.5% as the average contraction of the fibers released dry. The volume of water removed from a wet wool fiber on drying is about $\frac{1}{3}$ of the volume of the dry fiber. For ice [5], which is held together by a hydrogen bonded network, the Young's Modulus is 2.8×10^{10} dynes/cm.^{2} For the dry wool fiber, if we assume that the number of strained hydrogen bonds created by the removal of water is equivalent to $\frac{1}{3}$ of the number in ice, an effective Young's Modulus for these bonds would be $\approx 0.9 \times 10^{10}$ dynes/cm.^{2}, which is in agreement with the figure of $0.7_4 \times 10^{10}$ dynes/cm.^{2} obtained. However, no great significance should be attached to this agreement beyond the fact that the order of the two moduli was the same.

The steady increase of $(F_D - F_t)$ with strain (see Figure 3) to an asymptotic value when the strain is ~30% may indicate the presence of two distinct phenomena:

1. The bonds that are formed during drying, which oppose the extension, are becoming more oriented with strain. This would create a cooperative effect to increase the value of $(F_D - F_t)$ on drying.

2. Also, the increase in strain with its accompanying increase of water accessibility of the wool fiber would mean that on drying a greater number of bonds would be formed opposing the fiber extension.

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The Effect of Soil on the Photochemical Degradation of Cotton

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FIBER degradation may be the result of mechanical, chemical, or microbiological action by various agents, including the soil retained by textiles during use. However, precise information on the deleterious effect of soil is not available.

The term "soil" is generally used in textile literature to refer to all types of foreign matter accumulated by fabrics during use. Soil may be deposited by direct contact of the textile with a soiled surface, with air-borne or liquid-borne soil [5]. The source and the chemical composition of soil vary widely. Street sweepings, vacuum cleaner sweepings, and accumulations from air filters are considered to be typical in composition of the soil occluded by textiles [6, 8, 9].

It is possible that the soil which accumulates on a textile may accelerate photochemical degradation of fibers by acting as a photosensitizing agent. Photosensitization is of major importance in the photochemical degradation of textiles. This type of degradation occurs in ordinary light when a sensitizer is present that is capable of absorbing the light and passing the energy to the reacting fiber molecules. Various dyes, and substances such as zinc oxide and titanium dioxide, are capable of acting as sensitizing substances. The action of a sensitizer, as suggested by Egerton [4], is to absorb light energy and transfer it to the oxygen in the surrounding atmosphere. Activated oxygen is produced, which may react to form hydrogen peroxide in the presence of water vapor. Both the activated oxygen and hydrogen peroxide may cause degradation of textiles by oxidation.

The work of MacMillan and Bhattacherjee [7] suggests that lignin may also act as a sensitizer. They found that a volatile oxidizing agent, possibly hydrogen peroxide, was formed from lignin during irradiation of jute. The degradation of cotton was enhanced appreciably when the textile was irradiated in the vicinity of jute, and markedly when it was irradiated after impregnation with lignin.

The organic portion of ground soil, the loose surface material of the earth, contains a lignin complex. General reasoning concludes that there is a link between the lignin found in plant tissues and the lignin complex found in ground soil [3]. Since previous work [7] has shown that the lignin of jute acts as a photosensitizing agent, the lignin complex in ground soil may also have a photosensitizing action on cellulose.

In this study, cotton yarns were impregnated with an air-borne soil, a ground soil, and a lignin derivative of the ground soil. The effect of these soils on the photochemical degradation of the cotton was determined. The air-borne soil is considered to be typical of the soil accumulated by textiles during use. The ground soil chosen had a high organic content which would yield a high proportion of lignin derivative, and was classified as clay loam.

Procedure

The chemical analysis and particle size distribution of the ground and air-borne soils are listed in Tables I, II, and III. Foreign matter was removed from the ground soil, and it was pulverized until it would pass through a #10 wire-mesh screen. The air-borne soil was obtained from dry air filters in University buidings. It was sieved twice through a #40 wire-mesh screen.

A lignin derivative was extracted from the clay loam soil as follows. The portion of the soil that was soluble in 0.01 *N* NaOH was removed by centri-

TABLE I. Composition of Soils

Component	Air-borne soil, %	Clay loam soil, %
Moisture	3.5	6.6
Water-soluble	19.0	0.5
Organic matter	24.0	4.8
Inorganic matter	76.0	95.2

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TABLE II. Qualitative Spectrographic Analysis of Metals in Soils

Soil	Estimated percentage range			
	100–30	30–3	3–0.30	0.30–0.03
Air-borne	—	silicon iron	aluminum calcium zinc magnesium	lead sodium potassium titanium strontium
Clay loam	silicon	aluminum iron	sodium potassium calcium magnesium	titanium strontium

TABLE III. Particle-Size Distribution of Soils

Range, μ	Air-borne soil, %	Clay loam soil, %
0–1	9.0	40.0
0–2	18.0	44.0
2–50	49.0	42.0
50	33.0	14.0

fuging. The resulting supernatant was reduced to pH 1.9 by the addition of 0.1 *N* H_2SO_4, which brought the lignin derivative into a colloidal state. After dialization, this derivative was separated from the supernatant by centrifuging. The lignin derivative was resuspended by increasing the pH to 10.0 with 0.01 *N* NaOH. After the pH was adjusted to 7.0 with 0.1 *N* H_2SO_4, the volume was reduced 80% by evaporation. The optical density of this solution was found to be 1.360, as measured on a Klett Colorimeter using a green filter with 540 mμ maximum transmission.

A boiled-off, combed cotton yarn with a knitting twist, cotton count 40 : Z19/2 : S14 tpi, was used in all phases of this study. All yarn samples were taken from a single cone, and were prepared by wrapping the yarns around a white cardboard holder, $7\frac{1}{2}\times2\frac{1}{2}$ in. Yarn from the cone was wound around the cardboard in the long direction, thus permitting 100 yarns to be exposed. The samples were removed from the holders before soiling.

The lignin derivative was applied by submersing the yarn samples in 10 ml. of solution for 30 min. The solution was completely absorbed at the end of that time. After being air dried, the yarns were soiled in this same manner a second time.

The clay loam soil and the air-borne soil were applied to yarn samples by tumbling in the Launderometer for 45 min. at room temperature. One

TABLE IV. Corrected Apparent Fluidity (Rhes) of Cotton Yarns

Soil treatment	Fadeometer exposure		Aged	
	320 hr.	640 hr.	320 hr.	640 hr.
Control	4.63	9.88	0.28	0.27
Air-borne	6.56	11.57	0.28	0.28
Clay loam	—	9.29	—	0.25
Lignin-derivative	—	9.90	—	0.30

sample was placed in a glass jar containing 0.5 g. soil and 20 stainless steel balls. Each yarn sample retained enough soil to increase the weight of the yarn approximately 5%. The control yarns were tumbled in the same manner without soil.

The samples were returned to the cardboard holders before Fadeometer exposure, placed in metal specimen holder with $1\frac{3}{8}\times5$-in. openings, and straightened to ensure good coverage in the exposed area. All samples were exposed in an Atlas FDA-R Fadeometer for 320 or 640 hr. [1].

For each phase of this study, a second set of samples was prepared as described above. These samples were stored in the dark, under standard atmospheric conditions (65% RH, 70° F.), for a period of time equivalent to that of the Fadeometer exposure.

All yarn samples, both the soiled and the controls, were cleaned in the Launderometer before being evaluated for degradation. The yarn samples used in experimentation with the lignin derivative were washed for 5 min. in 200 ml. of a 0.05% neutral soap solution at 100° F., rinsed four times in distilled water, and air-dried. The yarn samples impregnated with the air-borne and the clay loam soils were washed three times, for 10 min. each, in 300 ml. of 0.1% neutral soap solution at 100° F., rinsed four times in distilled water between each of the three wash cycles, and air-dried. After the yarn was cleaned by these procedures, no soil was visible under microscopic examination (450×).

Strength measurements on the clean yarn samples were made on a constant-rate-of-load type instrument under standard temperature and humidity conditions. The distance between the clamps at the start of the test was 10 in. A minimum of 20 specimens was measured from each group of yarns.

Degradation of yarn samples was determined by measurement of cellulose fluidity. The yarns were dispersed in cupriethylene diamine hydroxide, using a modified version of ASTM D 539-53 [2]. Ost-

wald-type viscosimeters were used; the yarns were cut with hand shears to pass a #20 sieve. The ASTM procedure was modified in the following areas: the yarns were not extracted before dispersion, and a sample of approximately 0.1 g. was used for each individual determination. Fluidity is reported as corrected apparent fluidity in rhes.

Soil Characteristics

The metallic elements found in major proportions in the air-borne and clay loam soils used in this study are similar (Table II). However, the estimated percentage ranges for the minerals tend to be higher for the clay loam soil than for the air-borne. This is to be expected, since the clay loam soil has a higher percentage of inorganic material (Table I).

To study the composition of various soils encountered by textile materials, other workers have analyzed soil from air filters, city streets, and carpet sweepings [6, 8, 9]. In these analyses the soils were found to contain from 30 to 50% organic matter, to have a moisture content of less than 5%, and to have approximately 15% water-soluble matter. The air-borne soil used in this study had similar characteristics (Table I).

Ground soil which contains 5% organic matter, as did the clay loam, is considered to have a high organic content . However, soil considered typical of that encountered by clothing and household textiles has been shown to contain a much higher percentage of organic matter. Therefore, the air-borne soil is more nearly typical of the common types of soils encountered by textile products in everyday use than is the clay loam.

The soil accumulated on textiles varies widely in particle size, which ranges from submicroscopic to visible macroscopic. Of the two soils used in this study, the clay loam had a higher proportion of small particles (Table III). Approximately 50% of the clay loam had particles less than 2 μ in size, while less than 20% of the air-borne soil was in this range. These differences in particle size distribution may be attributed in part to the pulverization of the clay loam.

Sensitizing Action of Soils

The air-borne soil accelerated the photochemical degradation of cotton yarns. The cellulose fluidity values after 320 hr. of Fadeometer exposure were 6.6 rhes for the soiled yarns, as compared with 4.6 rhes for the unsoiled yarns (Table IV). Differences were also found between the soiled and unsoiled yarns after 640 hr. of exposure—11.6 rhes and 9.9 rhes, respectively. It is interesting to note that the greatest change in fluidity occurred during the first half (320 hr.) of the total exposure period. The fluidity values of the soiled, aged yarns were not found to differ significantly from the unsoiled, aged yarns. Therefore, the differences in fluidity of the exposed yarns appear to be the result of the photosensitizing effect of the air-borne soil.

Breaking-strength values of the yarns impregnated with air-borne soil did not parallel the fluidity results. No significant differences in strength were found between the exposed and aged soiled and unsoiled cotton yarns (Table V).

Fluidity measurements and breaking-strength values gave no indication that the lignin derivative had accelerated degradation after exposure for 640 hr. in the Fadeometer (Tables IV and V). Also, there were no differences in measurements between impregnated and unimpregnated yarns which had been aged in darkness under standard atmospheric conditions for an equivalent period.

The clay loam soil was also used for impregnation of a group of cotton yarns since it was possible that the lignin derivative had been altered by hydrolysis and oxidation during the alkaline-extraction process [3]. After Fadeometer exposure, no differences in strength or fluidity were found between the soiled and unsoiled samples. No differences were found between the soiled and unsoiled yarns after aging (Tables IV and V). It appears that this particular clay loam soil does not have a photosensitizing action on cotton yarns under the conditions used in this study.

TABLE V. Cotton Yarn Breaking Strength, g.

	320 hr.		640 hr.	
Soil treatment	$\bar{X}$	σ	$\bar{X}$	σ
Fadeometer exposure:				
Air-borne	350	49	276	29
Clay loam	383	43	290	28
Control	368	58	280	36
Aged:				
Air-borne	557	65	557	63
Clay loam	592	53	539	63
Control	508	114	553	87
Original	505	98		

The differences in fluidity values found among the yarns impregnated with the three soiling agents do not appear to have resulted from differences in hydrogen ion concentration. The pH values of the air-borne and clay loam soil suspension [10] were 6.3 and 5.6, respectively. The solution containing the lignin derivative was adjusted to pH 7.0 at the end of the extraction procedure.

Differences in particle size distribution between soils could affect their photosensitizing action, since a soil composed of small particles might be expected to have a greater photosensitizing action than one composed of larger particles. The results obtained in this study do not indicate that particle size was a contributing factor to photochemical degradation.

The chemical composition of the soils may have caused the observed differences in degradation, since the air-borne soil contained certain metallic elements that were not found in the clay loam soil. In addition, the composition and proportion of organic material in the two soils may be related to their photosensitizing action.

Summary

The effect of three soiling agents on the photochemical degradation of cotton was studied. Cotton yarns were impregnated with an air-borne soil, a ground soil, and a lignin derivative of the ground soil. After exposure to a carbon-arc light source, degradation was measured by fluidity and breaking-strength determinations.

Fluidity measurements indicated that the air-borne soil accelerated photochemical degradation of the cotton. There was no indication that the ground soil and the lignin derivative had a photosensitizing action. No differences in breaking strength values were found.

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The Dry Weight of Wool

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Abstract

A study has been made of the drying of wool *in vacuo*. The time required to reach the equilibrium weight decreases with increasing temperature of drying, and the equilibrium weight decreases with increasing temperature up to 140° C. The equilibrium weight obtained *in vacuo* is less than the weight obtained in air under the same conditions. The absolute dry weight of a wool sample is defined as that weight obtained on heating the sample *in vacuo* to 140° C. for at least 10 min.

The activation energy of drying increased markedly at low regains. From comparison with partially acetylated wool it was concluded that drying wool at low regains involves the removal of water from hydrophilic sites.

FURTHER investigation of the mechanism of absorption of water by wool requires more accurate data on the sorption isotherms than is available in the literature. The first requisite is a method of obtaining a reproducible weight of wool at zero relative humidity as the initial point of a wool–water isotherm. As will be evident later in this paper, a second requisite is a method of determining the weight of a wool sample from which all the water has been removed without degrading the wool; i.e., a method of determining the absolute dry weight.

Le Compte and Lipp [3] made a survey of methods commonly used for determining the moisture content of wool. They compared the efficiencies of the following methods of drying: a conditioning oven at 110° C., a suction dryer at 150° C., a forced draft dryer at 150° C., vacuum drying at room temperature, and removal of water by distillation with toluene. The various methods gave differences of moisture content of more than 0.5% regain for similar wool samples. From these results Le Compte and Lipp concluded that toluene distillation was the most reliable method of moisture determination, and vacuum drying over phosphorus pentoxide the least satisfactory because of the time involved.

The advantage of the method of removing water from wool by distillation with toluene, over most of the other methods, is that the wool sample is in an anhydrous medium. Any drying technique to yield values for the total moisture content should keep the surroundings of the wool anhydrous. Consequently the method of vacuum drying, which ensures anhydrous surroundings to the wool sample, should yield values of moisture content at least as high as the values obtained from the other methods discussed, if carried out at the same temperatures.

For the vacuum drying Le Compte and Lipp used a pressure of 4–5 mm. mercury, did not use elevated temperatures as in the other drying methods, and did not allow the drying sufficient time to reach final equilibrium. We, therefore, considered necessary a further study of vacuum drying with particular reference to obtaining high vacua and drying at elevated temperatures.

It is clear, however, that any method of moisture determination for a wool sample at elevated temperatures should take into account the possible degradation of the wool under the conditions of drying. Several workers have investigated this problem. Rutherford and Harris [9] heated moist wool to 105° C. in the absence of light for periods longer than 400 hr. without evidence of loss of cystine or total sulfur. However, degradation was initiated photochemically under the same conditions. Zahn [12] has reported that wool does degrade slowly in boiling water, some 4% dissolving in 24 hr. Stirm and Rouette [11] have shown that this rate of decomposition becomes more rapid at temperatures above 100° C. On the other hand, they found the extent of degradation to be a function of moisture content and very much reduced for dry wool. Bull [2] found discoloration of moist wool heated overnight in a vacuum oven.

Similarly, Mazingue and van Overbeke [7] have

reported that heating of wool in the absence of water vapor as high as 160° C. brings about only slow degradation.

It is worth noting that Zahn [13] found no degradation of dry horsehair below 150° C., and that Mechan and Olcott [8] heated dry hoof keratin above 153° C. before general degradation took place. It seems, therefore, that dry keratinous materials show strong resistance to heat.

Experimental Method

Samples of wool of about 50 mg. weight, teased out to occupy a volume of at least 10 cm^3., were suspended from quartz helical springs in glass sorption chambers which could be evacuated to pressures less than 10^{-3}mm. mercury through a liquid air trap. The sorption chambers were immersed in a liquid thermostat controllable to ±0.01° C. Sensitivities of the helical balances were of the order of 5 mm. extension per milligram load and the extensions were measured accurately to 0.01 mm. by a cathetometer. Weight changes of 2.0×10^{-6} g. corresponding to regain changes of less than 0.005% could therefore be detected. The sensitivity of each spring was measured at 20° C. and the variation of sensitivity with temperature determined. The results were found to be in excellent agreement with the calculated temperature dependence of sensitivity using the formula of Ernsberger [4].

The wool used in the following experiments was pen-grown Merino which had been washed with cold petroleum ether and thoroughly rinsed with distilled water until the pH was neutral and did not change after standing overnight in the final rinse water. Corriedale wool was also used in some experiments; no difference in behavior was noted except an increase in time to reach equilibrium regain because of the greater fiber diameter.

Results

Rates of Drying

A wool sample was allowed to equilibrate with water vapor at a chosen temperature and 100% RH. The rate of drying was determined at that temperature by evacuating the sorption chamber and following the change of spring length as a function of time. The drying time was that after which no further change of spring length could be detected. Evacuation was continued for an equal length of time to ensure that equilibrium had been attained. The weight of wool was then the equilibrium dry weight under the experimental conditions. The pumping speed was such that even at high temperatures and high humidities the rate of removal of water vapor

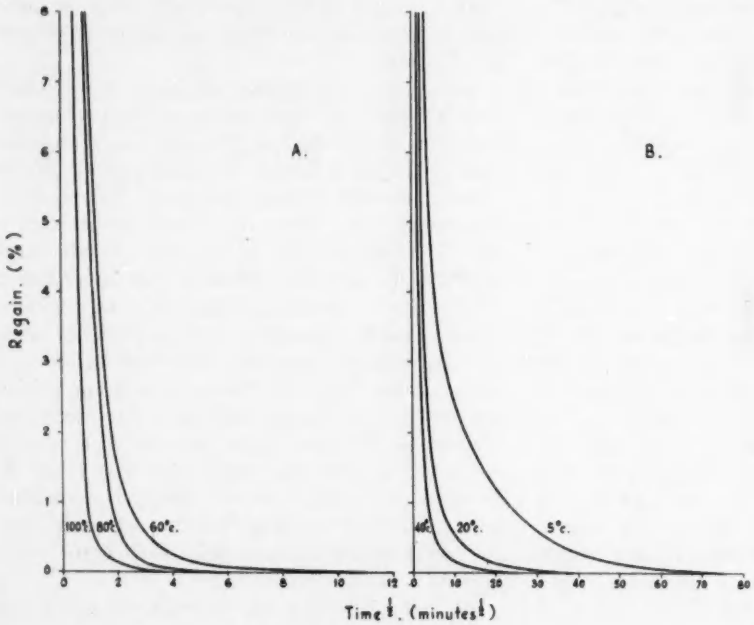

Fig. 1. Drying curves at six temperatures.

from the sorption chamber was not a limiting factor in the rate of drying of the wool. The wool was teased into a loose bundle so that cooling due to the endothermic nature of drying could be effectively countered by radiation of heat from the side walls of the sorption chamber. The efficiency of this method of keeping the temperature constant was checked experimentally by altering the density of packing by a factor of ten; no change was observed in the shape of the drying curves.

In Figure 1 the regain of a wool sample is shown as a function of $(\text{time})^{\frac{1}{2}}$ for six temperatures between 5° C. and 100° C. Each experiment has been repeated at least six times. It will be seen that the time taken to reach equilibrium with Merino wool varies from 72 hr. at 5° C. to 8 min. at 100° C. All curves have been plotted on the basis of the equilibrium dry weight.

The Absolute Dry Weight

A wool sample was vacuum dried to equilibrium at 5° C.; then the temperature was raised to 200° C. with continuous evacuation. The loss of weight as a function of temperature is shown in Figure 2. The apparent regain of the sample at each temperature was calculated taking the weight at 20° C. as the dry weight of the wool sample. The temperature was held constant at intervals for a length of time equal to the drying time at that temperature, indicated by Figure 1, to ensure equilibrium. For temperatures above 100° C. an interval of 10 min. was allowed before reading the spring extension for that temperature. It will be seen that the loss of weight is almost linear with temperature up to 100° C., but with further temperature increase the loss of weight is less. Between 140° C. and 160° C. the weight remains almost constant, being then 0.3% less than at 5° C. Above 160° C. the wool loses weight rapidly; discoloration was observed at 170° C., indicating that degradation of the wool was occurring. The discoloration of wool noted by Bull [2] at 137° C. was observed after overnight heating. However, 1-g. samples of clean carded Merino wool heated to 140° C. *in vacuo* for periods of up to 20 min. could not be distinguished by eye from similar untreated wool. Measurements on these samples in the "Color Eye" apparatus showed a drop of only 4% on the ζ tri-stimulus coordinate, which was below the limit of visual detection.

Other samples from the same wool were heated

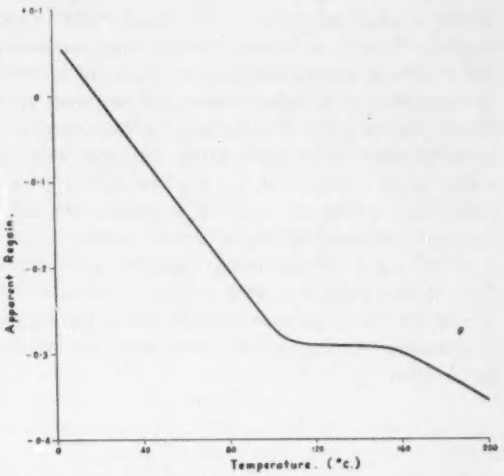

Fig. 2. Variation of the vacuum dry weight of wool with temperature. Zero regain is the equilibrium dry weight at 20° C.

in vacuo to various temperatures for 30 min., cooled to 20° C., and resubmitted to a standard treatment of saturation with water vapor and drying to equilibrium. Samples which had been heated to temperatures up to 150° C. showed no loss of weight between the first and second standard treatments. Samples which had been heated to 160° C. showed a very small decrease of weight after the second standard treatment. Heating to higher temperatures resulted in considerable weight losses. For instance, heating at 200° C. for 30 min. decreased the weight of a wool sample by 3%.

Therefore, the heating of dry wool *in vacuo* to temperatures as high as 150° C. for periods up to 30 min., as in the above experiment, does not cause permanent weight loss. However, heating to temperatures above 160° C. even for very short periods brings about permanent damage as indicated by loss of weight.

It was noted that on raising the temperature the dry weight of the wool sample quickly fell to the equilibrium value at the higher temperature. The time required was considerably less than the time to dry the wool sample at the higher temperature, from a regain equivalent to the difference in dry weights at the two temperatures. For example, raising the temperature from 40° C. to 60° C. decreases the equilibrium dry weight by an amount equal to 0.04% regain, and the new equilibrium dry weight is attained within 30 min. On the other hand, vacuum

drying a wool sample at 60° C. from 0.04% regain requires 2 hr. It is probable that the removal at 60° C. of the water remaining in the wool at 40° C. is dependent on sufficient opening of the wool structure, which would be achieved by the increase of temperature. This observation indicates that the water which remains in the wool at the lower temperature is not the last water to be removed in drying from saturation at the higher temperature.

In the light of the above considerations, it was decided that heating a wool sample to between 140° C. and 150° C. with constant evacuation for 10 min. is a satisfactory means of determining the absolute dry weight.

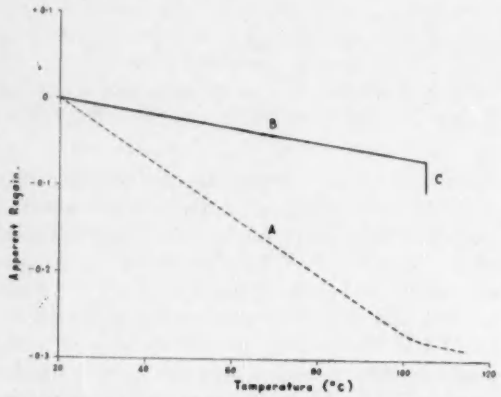

Fig. 3. Variation of the dry weight of wool with temperature. A: heating with constant evacuation; B: heating in dry air to 105° C.; C: evacuation at 105° C.

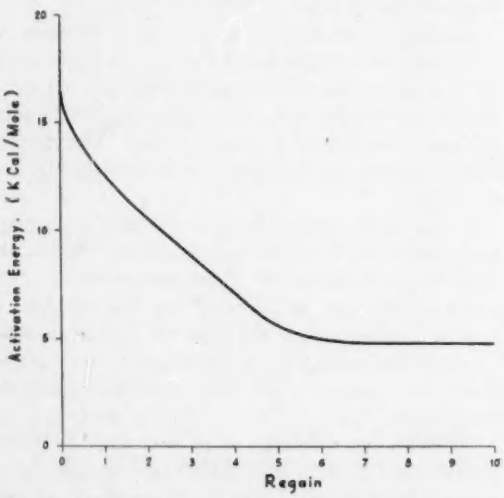

Fig. 4. Activation energy of drying as a function of regain.

Drying in Air

A wool sample was dried *in vacuo* from saturation regain at 20° C. to its equilibrium dry weight. Air, dried by bubbling through concentrated sulfuric acid and passing slowly through a trap immersed in liquid air, was admitted to the sample. The spring length was corrected for the buoyancy of the sample in air. No increase in the weight of the wool sample was observed. The sample was then heated in the air to 105° C. (Curve B of Figure 3), and after 30 min. the chamber was evacuated at 105° C. (Curve C of Figure 3).

The chamber was cooled to 20° C., the sample brought to saturation regain, and the above sequence of operations repeated with the same effect. In addition, another wool sample which had been saturated and dried at 20° C. was heated *in vacuo* to 105° C. (Curve A of Figure 3). This sample was cooled to 20° C., saturated, and dried *in vacuo* before heating in air to 105° C. The effect was the same as with the previous sample (Curve B). The sample was again cooled to 20° C., saturated, dried *in vacuo*, and heated *in vacuo* to 105° C., again giving Curve A. From this evidence it is clear that the lower dry weight obtained by heating *in vacuo* is not due to the removal of volatile material from the wool samples. Further work on the difference in the dry weights obtained by drying in air or vacuum is being undertaken.

The Activation Energy of Drying

The rate of drying at a chosen regain and temperature can be calculated from the slope of the appropriate drying curve of Figure 1. The rate of water removal at twelve regain levels was determined for each of six temperatures in the range 5°–100° C. For each regain level the activation energy of drying was calculated from the Arrhenius equation:

$$\text{Rate} \propto e^{-E/RT}$$

where R = the gas constant = 1.987 cal/° A/mole, T = absolute temperature, and E = the activation energy of drying. The value of the activation energy of drying will be the sum of the energy contributions for the release of water molecules from the keratin and their transport to and removal from the fiber surface.

It has been shown (Figure 2) that the equilibrium dry weight of a wool sample decreases with increasing temperature and that the additional water is

removed quite readily at the higher temperature. Therefore it is preferable, in order to compare rates of drying in the low regain region, to calculate the regain on the basis of the equilibrium dry weight rather than the absolute dry weight of the wool.

The variation of activation energy of drying with regain is illustrated in Figure 4. It can be seen that at low regains the activation energy is dependent on the regain level at which it is calculated. As the regain falls below 6.5% there is an increase in the activation energy which becomes very marked at lower regains, rising to values of 15–16 kcal./mole at regains less than 0.2%. At regains above 6.5% the activation energy remains almost constant at 4.8 kcal./mole. It was not possible to make accurate measurements of the rate of drying at regains above 10% for the higher temperatures of drying, but the activation energy appeared to remain constant over a wide variation of regain.

Discussion

The lowest dry weight of a wool sample that can be obtained without degradation of the fibers has been defined as the absolute dry weight. It is apparent from the curves of Figure 1 and Figure 2 that continuous evacuation of the surroundings of a wool sample is not sufficient to completely dry the sample unless carried out at elevated temperatures. The dry weight decreases with increasing temperature up to 140° C., and it has been shown that dry wool heated up to 150° C., at least for periods up to 30 min., showed no loss of weight or alteration of desorption behavior on subsequent drying from saturation at 20° C. Therefore the heating of wool above 140° C. but below 150° C. yields the lowest value of the dry weight *in vacuo*.

It was observed that the heating of a wool sample in the presence of dry air (Figure 3) left the wool with a higher dry weight than if the same sample had been heated *in vacuo*. Therefore, any method of absolute dry weight determination should exclude air as well as all traces of water from the system containing the wool sample. Precise values of the moisture content of wool will not be obtained using conditioning ovens, suction dryers, or forced draft dryers because in each case air and low concentrations of water vapor are present.

The method of determining the water content of a wool sample by distillation in toluene, which Le Compte and Lipp found to yield high values of the water content, is limited by the fact that the temperature can be raised only to 110° C. and is, therefore, inadequate for complete removal of water from the fibers. Some liquid with a higher boiling point than toluene could be substituted, but the experimental difficulty of determining accurately the condensed water makes the method unsatisfactory for small samples.

Drying at room temperature over phosphorus pentoxide in a dessicator, which has been a popular laboratory method of determining the dry weight of a wool sample, is both tedious and inaccurate. Of the drying methods considered, vacuum drying at elevated temperatures yields the lowest dry weight of a given wool sample and the most accurate estimation of the original water content.

It became apparent in the course of the work that the dry weights obtained under any set of conditions were a function of the previous treatment of the wool; e.g., the equilibrium dry weight could be altered by dosing to saturation or drying with a series of small RH changes instead of a 100% RH change. These observations will be fully discussed in a later paper. However, irrespective of the previous drying history of a wool sample, the dry weight changes depicted in Figures 2 and 3 will be obtained on heating the sample.

The measured activation energy of drying must include a number of temperature-dependent mechanisms which will also be dependent on regain to some extent. Removal of water from the wool fibers involves transport processes as well as bond breakages. The transport process will be influenced by structural configuration, entropy of water molecules, and the concentration of water in the fiber. Although the contribution of each of these factors cannot be determined in this experiment, at low regains their combined effect is likely to be small compared with the binding energy.

Speakman [10] has postulated that on absorption some water molecules are attached to specific sites in the wool fibers with an energy of bonding of 5.8 kcal./mole, and additional water is absorbed with very little energy of bonding. The hydrophilic groups available for reaction with water molecules in keratinous materials are hydroxyl (-OH), carboxylic (-COOH), basic ($-NH_2$), and acid amide ($-CO\cdot NH_2$) groups. The heats of hydration of these groups have been given by Speakman [10] as 5.7 kcal./mole for -OH groups, 7.4 kcal./mole for $-COO^-$ ions, and 16.8 kcal./mole for NH_3^+ ions. No figure is available for the heat of hydration of the

acid amide group, but it has been reported by Green [5] that the acid amide groups of proteins are too weakly polar to adsorb water.

The activation energy of drying is constant from 6.5% to 10% regain at 4.8 kcal./mole (Figure 4), which coincides with the value given by King [6] for the activation energy of diffusion through horn keratin at 16% regain. Since the values of the heats of hydration of the hydrophilic side chains in keratin are greater than 4.8 kcal./mole, it is unlikely that removal of water molecules from these side chains at regains greater than 6.5% is important. It is therefore probable that transport processes are the major rate-controlling factor of drying above 6.5% regain for keratinous materials.

Below regains of 6.5%, the binding energy is an increasingly significant part of the measured activation energy of drying. It would be difficult to assign water molecules to specific sites at a given regain, as it is likely that local variations of regain exist throughout the keratin. The measured activation energy and regain must both be regarded as averages for the material.

King [6] has reported an activation energy of sorption of 7.5 kcal./mole for the sorption of water vapor by a horn keratin membrane at unspecified low regains; this would correspond to a regain of about 4% from Figure 4. As both the (-OH) and (-COOH) groups have heats of hydration greater than 4.8 kcal./mole, it is probable that removal of water from these sites contributes to the increased activation energy of drying below 6.5% regain. There has been no suggestion in the literature that in wool or other polymers the process of water transport involves higher energies at low concentrations of water. The striking increase in the activation energy of drying near zero regain therefore suggests that a further mechanism of water removal comes into action in this region. It is suggested that this mechanism is the removal of water from specific high energy sites in the wool. The heat of hydration of NH_3^+ ions (16.8 kcal./mole) is much greater than that of any of the other hydrophilic side chains in wool [10], and is of the same order as the observed activation energy of drying at 0.1% regain. Therefore, it is likely that, at very low regains (less than 0.5%), water molecules are held largely on the high energy sites and that the activation energy of drying consists principally of the energy needed to break water–NH_3^+ bonds.

If wool near zero regain has most of the water held on NH_3^+ ions, one would expect a marked change in the rate of drying, at very low regains, of wool in which all the NH_3^+ ions had been chemi-

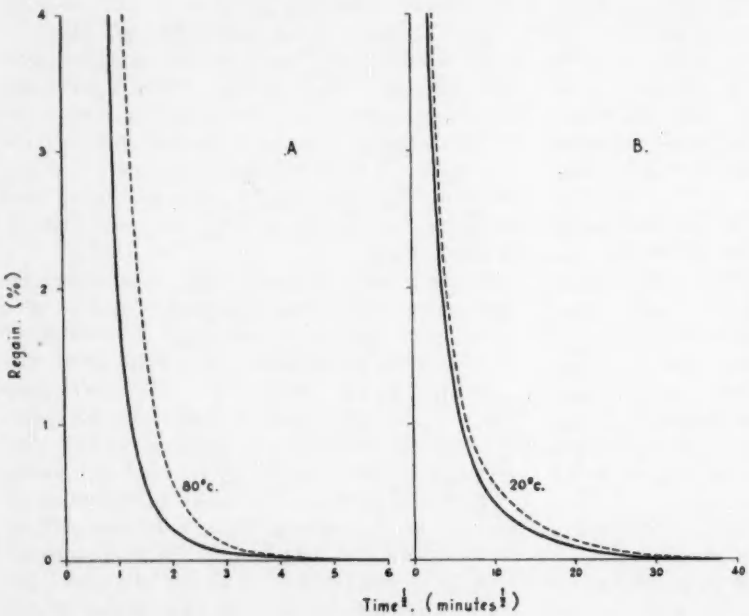

Fig. 5. Drying curves. ——— Acetylated wool; - - - - - - - normal wool.

cally blocked. Such a modified wool would have water molecules attached to sites of much lower energy than NH_3^+ ions. Therefore the energy required to remove water at low regains would be reduced, and the rate of water removal would be faster for the modified wool. Hence the time to reach equilibrium dry weight would be less. Complete blocking of NH_3^+ ions in wool is impractical, so the effect of partial blocking must be considered. If only some 70% of NH_3^+ ions are blocked, there still remain some high energy sites in the unmodified wool, and the time to reach equilibrium dry weight is unchanged. However, in a modified wool sample at any regain, the percentage of water molecules attached to NH_3^+ ions compared to the total water content of the sample will be less than for normal wool at the same regain. Therefore at low regains the rate of drying of the modified wool will be less than that of the normal wool. The activation energy of drying will also be less for the modified wool.

A qualitative test of the foregoing was made by taking drying curves of modified wool. The wool was acetylated by the I. G. Farben method as reported by Alexander and Hudson [1]. Figure 5 shows the drying curves at two temperatures for both a normal and an acetylated wool. At each temperature the acetylated wool has a lower regain than the normal wool at a corresponding time. In the later stages of drying the rate of water removal of the modified wool is much slower than for normal wool, while the time to reach equilibrium dry weight is the same for both. An approximate activation energy of drying was calculated from drying curves of acetylated wool at four temperatures between 20° C. and 80° C. For regains less than 3% this activation energy was lower than that of normal wool; at 0.5% regain its value was 12 kcal./mole compared with 14 kcal./mole for normal wool.

Thus the expected effects of partially blocking the NH_3^+ ions in wool have been observed; this lends support to the suggestion that, near zero regain, water is held in wool mainly on high energy sites, which are probably NH_3^+ ions.

Conclusion

The length of time required to vacuum-dry a wool sample to an equilibrium dry weight varies with the temperature of drying. For Merino wool the time ranges from 72 hr. at 5° C. to less than 8 min. above 100° C.

The equilibrium dry weight of a wool sample decreases with increasing temperature up to 140° C. At 160° C. and higher temperatures, a dry wool sample loses weight because of degradation. The absolute dry weight of a wool sample is here defined as that weight attained by the sample heated *in vacuo* at a temperature greater than 140° C. but less than 150° C. for a period of 10 min.

Part of the absorbed water is strongly bound to specific sites in the wool fibers.

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Cross-Linking of Partially Cyanoethylated Cotton[1]

Part I: Carbamoylethylation and Formaldehyde-Curing

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Abstract

By means of the hydrogen peroxide method, the carbamoylethylation of partially cyanoethylated cotton containing a low percentage of nitrogen appeared to be achieved to some extent without almost any damage. By formaldehyde-curing (110–150° C.) in the presence of acid catalyst such as ammonium chloride or dimethylaniline hydrochloride, the crease resistance of partially carbamoylethylated cotton fabrics, accompanied by a corresponding loss in the tensile strength and elongation, was improved over that of the cyanoethylated cotton. However, the improvement was less than that of the unmodified cured cotton. By curing (110–130° C.) with a moderately weak acid catalyst such as secondary ammonium phosphate, the crease resistance of the carbamoylethylated cotton was improved to some extent without so great a decrease in the tensile strength and elongation. Therefore, in the formaldehyde-curing of partially carbamoylethylated cotton fabrics the formation of a long chain of N-methylene bis ethyleneamide cross link between different cellulose molecules was deduced. An ammonium acetate catalyst was too weak to give any improvement. The good dyeing properties of cyanoethylated cotton have been retained after carbamoylethylation and formaldehyde-curing.

Introduction

Formaldehyde has been of interest as a cellulose cross-linker available to improve crease resistance. However, formalization is usually apt to be accompanied by much loss in tensile and tear strength and elongation. It has been accepted generally that the unfavorable effects may be due to the shortness of the formal cross link and the acid hydrolysis of the cellulose [4, 6].

Therefore, the attention of the present authors was turned to partially cyanoethylated cotton, which has a certain degree of acid resistance and the chemical reactivity of —CN groups. It seems probable that the introduction of the long chain of N-methylene amide cross links into cotton cellulose is achieved by the direct formaldehyde-curing or the carbamoylethylation and subsequent formaldehyde-curing of the partially cyanoethylated cotton, using an acid catalyst. In the case of the direct formaldehyde-curing of cyanoethylated cotton, a part of —CN groups may be hydrolyzed to amide groups and form N-methylene amide cross links between amide groups or amide and —OH groups. If the cyanoethylated cotton could be prior-carbamoylethylated with the hydrogen peroxide treatment, the formation of N-methylene amide cross links in the formaldehyde-curing might be greatly facilitated [2, 5, 8, 9]. In the above treatments, although the formal cross links may be formed between the remaining free —OH groups, formation of the longer chain of N-methylene bis ethyleneamide cross links is also possible to some extent. In using a weaker catalyst, it seems probable that the latter predominantly takes place, because of a greater reactivity of amide groups. For cyanoethylated cotton fabrics, it would be expected to improve properties such as crease resistance without impairing the tensile and dyeing characteristics.

[1] Presented at a meeting of the Society of Textile and Cellulose Industries, Tokyo, Japan, May 27, 1959.

Experimental

Materials

The cotton was desized, scoured, and bleached calico cloth (30's).

Cyanoethylation

Cyanoethylation was carried out by two-step liquid or vapor phase procedure. The procedures consist essentially of padding the fabrics to 80–100% pickup of solutions of sodium hydroxide (1–5%) and treating with acrylonitrile for 30–40 min. at 50° C. or

65° C. Cyanoethylated cotton samples varying in nitrogen content from 2 to 4.4% were prepared.

Carbamoylethylation

The partially cyanoethylated cotton samples (5–10 g.) were treated with aqueous 3% hydrogen peroxide solution (500 ml.) at 40° C. and pH 9.1–9.3 controlled with sodium hydroxide and sodium phosphate for various periods of reaction (15–120 min.). The treated samples were washed with water, 0.1% hydrochloric acid, and then rewashed thoroughly with water. The nitrogen content was determined by the semimicro Kjeldahl procedure [1].

Infrared Absorption Measurements

Infrared absorption spectra by means of the KBr disc method were measured to confirm the formation of $—CO \cdot NH_2$ groups by carbamoylethylation.

Formaldehyde Curing

The unmodified, cyanoethylated, or carbamoylethylated cotton samples were soaked in the aqueous solutions containing 12% formaldehyde and 0.2–2.0% acid catalyst (ammonium chloride, dimethylaniline hydrochloride, secondary ammonium phosphate, or ammonium acetate) for 10 min. at room temperature, pressed out to about 100% pickup of the solution, and cured for 10 min. at 110–150° C. in the electric oven. The cured samples were washed with hot water until the free formaldehyde was removed. The bound aldehyde was not determined.

Test Procedures

All tests were performed at 20° C. and 65% relative humidity. Tensile strength and elongation of the fabrics were determined by the Schopper tester. Crease resistance was determined by the T. B. L. method, in which the opening distance of the folded and pressed specimen (1×4 cm.) is measured. With a few samples, tear strength by the Elmendorf's pendulum tester, flex abrasion strength by the Custom Universal Wear Tester, and stiffness by the Clark's tester were determined. The moisture regain and dyeing properties were also tested.

Discussion and Results

Confirmation of Carbamoylethylation

The partially cyanoethylated cotton containing 2.7% N was treated with the aqueous 3% hydrogen peroxide solution for 10, 20, 40, 60, and 120 min. at 40° C. and pH 9.1. As shown in Table I, a small decrease of nitrogen content was found. However, this was insufficient to confirm carbamoylethylation. Therefore, infrared absorption measures were attempted; some of the results are shown in Figure 1. A KBr disc of the unmodified or partially cyanoethylated cotton was prepared from 200 mg. of a mixture containing 3 mg. sample and 400 mg. KBr. A disc of the carbamoylethylated cotton was prepared from 200 mg. of the mixture containing 2 mg. sample and 350 mg. KBr. It is demonstrated undoubtedly

TABLE I. Effects of Hydrogen Peroxide Treatment of Cyanoethylated Cotton Fabrics on the Nitrogen Content and Physical Properties

Time of treatment, min.	Nitrogen content, %	Tensile strength, Kg./cm.	Elongation, %	Crease resistance, %
Unmodified cotton		7.16	10.6	40.0
Cyanoethylated cotton				
0	2.73	8.60	13.2	50.8
10	2.59	8.64	12.9	51.3
20	2.65	6.84	13.5	51.3
40	2.54	8.50	11.9	52.8
60	2.60	6.22	12.0	52.3
120	2.60	6.48	11.4	53.3

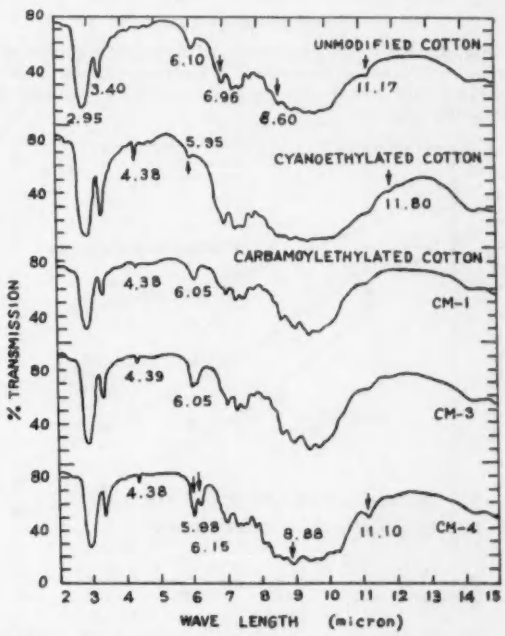

Fig. 1. Infrared spectra of unmodified, cyanoethylated, and carbamoylethylated cotton (CM-1, 3, and 4 were carbamoylethylated for 10, 40, and 60 min. respectively).

that the treatment of partially cyanoethylated cotton with hydrogen peroxide introduces into the spectra the same amide band at 6.0μ arising from the C=O stretching as that which has been found in direct carbamoylethylation of cotton by reaction with acrylamide [7] and decreases the intensity of the —CN band at 4.4μ. The 6.1μ band observed in the unmodified cotton is due to the absorbed water [7]. The intensity of the amide band appears to increase with the duration of reaction. However, complete carbamoylethylation has not been reached even in the treatment of 60 or 120 min. as shown by some remaining —CN band.

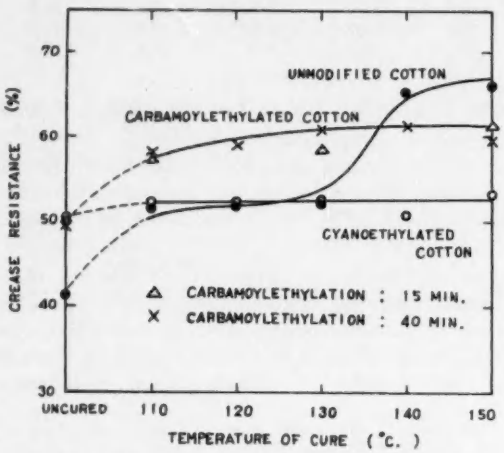

Fig. 2. Effect of temperature of formaldehyde cure on crease resistance of unmodified, cyanoethylated, and carbamoylethylated cotton fabrics using secondary ammonium phosphate catalyst.

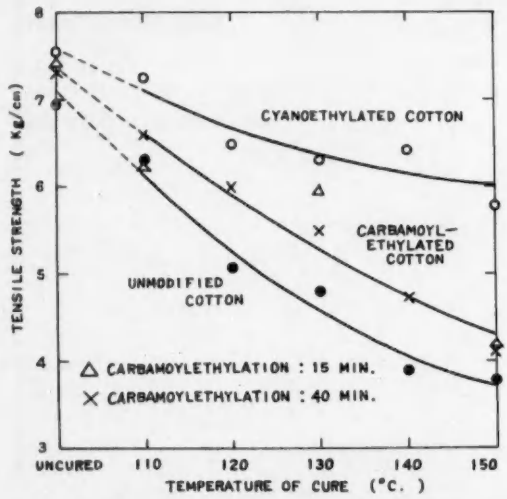

Fig. 3. Effect of temperature of formaldehyde cure on tensile strength of unmodified, cyanoethylated, and carbamoylethylated cotton fabrics using secondary ammonium phosphate catalyst.

Changes of Physical Properties by Carbamoylethylation

Changes of the tensile strength, elongation, and crease resistance by carbamoylethylation of the cyanoethylated cotton fabrics were measured. The results are shown in Table I. It is observed that the fabrics have not suffered much oxidation damage.

Physical Properties of Formaldehyde-Cured Samples

Ammonium chloride catalyst. Unmodified, 2.11% N cyanoethylated (8.86 mole % degree of cyanoethylation) and 2.05% N carbamoylethylated (40 min. of carbamoylethylation) cotton fabrics were formaldehyde-cured using 0.2–1.2% ammonium chloride padding solution (pH 3.1–2.8). The effects of curing on tensile strength, elongation, and crease resistance are shown in Table II.

Expectedly, the carbamoylethylated cotton is improved in crease resistance by the formaldehyde-curing much more than the cyanoethylated cotton,

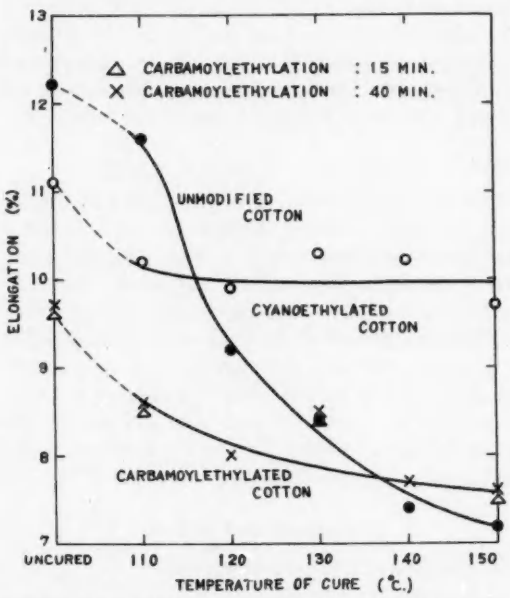

Fig. 4. Effect of temperature of formaldehyde cure on elongation of unmodified, cyanoethylated, and carbamoylethylated cotton fabrics using secondary ammonium phosphate catalyst.

indicating the formation of a certain degree of N-methylene amide cross link. However, the improvement is not equal to that of the unmodified cured cotton. This may perhaps be attributed to a difference of the amount, not length, of cross link. In the carbamoylethylated cotton, although formation of the short formal cross link chain may exist, formation of the long cross link chain of N-methylene amide is considered to be existent to a certain extent. The losses of tensile strength and elongation correspond to the increase of crease resistance and may structurally be responsible for the increased elastic recovery, as pointed out by Gagliardi and Gruntfest and others [3, 4]. Here, in addition, the resistance for acid hydrolysis might be related. The increase of crease resistance and the losses of tensile strength and elongation tend to level over 0.5% concentration of catalyst and 120° C. cure.

Our further work was directed toward finding a weaker catalyst which causes the amide cross link predominantly, with far lower formation of formal cross link.

Dimethylaniline hydrochloride catalyst. The same cyanoethylated and carbamoylethylated cotton sam-

TABLE II. Effects of Formaldehyde-Curing on Crease Resistance, Tensile Strength, and Elongation Using Ammonium Chloride Catalyst

Sample	Conc. of catalyst, %	Temp. of cure, °C.	Tensile strength, Kg./cm.	Elongation, %	Crease resistance, %	Discoloration
Unmodified cotton	uncured		7.20	11.6	44.2	
	0.2	110	3.42	5.6	91.4	
	(pH 3.10)	130	3.22	5.2	93.6	
		150	3.20	5.2	93.4	
	0.5	110	3.28	5.4	92.6	
	(pH 2.95)	130	3.10	5.0	92.3	
		150	2.76	4.8	93.6	slight yellowish
	1.2	110	2.94	4.0	94.0	
	(pH 2.80)	130	too weak to test		94.2	yellowish brown
		150	too weak to test		89.0	yellowish brown
Cyanoethylated cotton	uncured		8.10	11.9	50.6	
	0.2	110	4.40	7.6	66.8	
		130	4.24	7.4	70.0	
		150	4.00	7.2	72.9	
	0.5	110	4.08	7.3	72.6	
		130	3.67	6.9	77.8	
		150	3.42	6.7	80.4	
	1.2	110	3.72	6.9	74.3	
		130	3.50	6.4	76.3	
		150	3.30	6.1	81.0	
Carbamoylethylated cotton	uncured		7.10	11.0	51.2	
	0.2	110	3.66	7.1	81.0	
		120	3.56	7.0	83.8	
		130	3.40	6.9	82.4	
		140	3.40	6.8	82.8	
		150	3.30	6.4	84.3	
	0.5	110	3.54	6.9	82.5	
		120	3.50	6.9	82.0	
		130	3.35	6.5	83.2	
		140	3.30	6.2	84.3	
		150	3.28	6.2	88.4	
	1.2	110	3.35	5.9	90.8	
		120	3.33	5.7	91.3	
		130	3.30	5.7	86.5	
		140	3.33	5.8	86.8	
		150	3.20	5.6	87.5	

ples as used above were formaldehyde-cured using 0.25% dimethylaniline hydrochloride padding solution (pH 2.95). The effects on the physical properties are similar to that of ammonium chloride catalyst, except there is a somewhat lower increase in crease resistance and less loss in tensile strength and elongation, as shown in Table III.

Secondary ammonium phosphate catalyst. As the next weaker catalyst, secondary ammonium phosphate was selected. By use of the same 2.11% N cyanoethylated cotton as used above, the carbamoylethylation was carried out for 15 and 40 min. at 40° C. and pH 9.1. These products contain 2.08 and 2.06% N respectively. The formaldehyde-cur-

TABLE III. Effects of Formaldehyde-Curing on Crease Resistance, Tensile Strength, and Elongation Using Dimethylaniline Hydrochloride Catalyst

Sample	Temp. of cure, °C.	Tensile strength, Kg./cm.	Elongation, %	Crease resistance, %	Discoloration
Unmodified cotton	uncured	7.20	11.6	44.2	
	110	3.30	6.2	90.1	pale blue
	130	3.25	5.4	91.3	pale blue
	150	3.04	4.8	91.0	pale blue
Cyanoethylated cotton	uncured	8.10	11.9	50.6	
	110	5.85	8.8	60.9	
	130	5.60	8.2	64.8	
	150	4.18	7.6	71.5	pale blue
Carbamoylethylated cotton	uncured	7.10	11.0	51.2	
	110	4.46	7.8	72.6	
	120	3.90	7.4	74.0	
	130	3.68	7.2	74.2	
	140	3.53	6.8	77.6	pale blue
	150	3.10	6.4	77.0	pale blue

TABLE IV. Effects of Formaldehyde-Curing on Crease Resistance, Tensile Strength, and Elongation Using Secondary Ammonium Phosphate Catalyst

Sample	Temp. of cure, °C.	Tensile strength, Kg./cm.	Elongation, %	Crease resistance, %	Discoloration
Unmodified cotton	uncured	6.95	12.2	41.3	
	110	6.30	11.6	51.5	
	120	5.08	9.2	51.8	
	130	4.80	8.4	52.0	
	140	3.90	7.4	65.3	
	150	3.80	7.2	66.0	slight yellowish
Cyanoethylated cotton	uncured	7.55	11.1	50.3	
	110	7.25	10.2	52.0	
	120	6.48	9.9	52.0	
	130	6.30	10.3	52.5	
	140	6.40	10.2	50.8	
	150	5.78	9.7	53.3	slight yellowish
Carbamoylethylated cotton (15 min.)	uncured	7.43	9.6	50.0	
	110	6.25	8.5	57.7	
	130	5.95	8.4	58.5	
	150	4.20	7.5	61.3	pale yellow
Carbamoylethylated cotton (40 min.)	uncured	7.30	9.7	49.5	
	110	6.60	8.6	57.9	
	120	6.00	8.0	59.0	
	130	5.50	8.5	60.8	
	140	4.73	7.7	61.3	pale yellow
	150	4.13	7.6	59.8	pale yellow

ing was done with the padding solution containing 1.5% of secondary ammonium phosphate (pH 3.1). The effects on the physical properties are given in Table IV and Figures 2, 3, and 4.

Generally, the increase in crease resistance and the losses in tensile strength and elongation are less than in the usage of ammonium chloride or dimethylaniline hydrochloride catalyst. However, it is interesting that the crease resistance in the unmodified cotton is distinctly improved by curing only above 130° C.; in the cyanoethylated cotton, slightly improved over all temperatures of cure; and in the carbamoylethylated cotton, greater improved than any others in the 110–130° C. range, tending to level above a 130° C. cure. It appears to show that the carbamoylethylated cotton has introduced predominantly the long chain N-methylene bis ethyleneamide cross link, the cyanoethylated cotton introduced hardly any cross link, and the unmodified cotton introduced a significant formal cross link barely above the 130° C. cure.

It is also noteworthy that the decrease in elongation caused by curing seems to correspond to the increased crease resistance; however, the loss of tensile strength does not, being greatest in the unmodified cotton, moderate in the carbamoylethylated cotton, and least in the cyanoethylated cotton over all temperatures of cure.

From these results, it is suggested that introducing the longer cross link chain improves the crease resistance–tensile strength relationship rather than the crease resistance–elongation relationship, though some effect of acid resistance of —CN groups has to be considered.

The effect of duration of carbamoylethylation on the physical properties of the cured fabrics was not observed between the reaction times of 15 and 40 min.

Ammonium acetate catalyst. As the most weak catalyst, ammonium acetate was used. Using 2.73% N cyanoethylated cotton, carbamoylethylation for 15 min. at 40° C. and pH 9.3 gave a 2.57% N product. The formaldehyde-curing was done at 110° C., using 0.5–2% ammonium acetate solution (pH 4.45–4.30). The physical properties of the cured fabrics are shown in Table V.

Also, Table VI shows the effects of varying the cure temperature using 0.5% ammonium acetate padding solution (pH 4.2). The sample used here was the one of 2.04% N carbamoylethylated (40 min., 40° C., and pH 9.1) from 2.11% cyanoethylated cotton.

TABLE V. Effects of Formaldehyde-Curing on Crease Resistance, Tensile Strength, and Elongation; Varying Concentration of Ammonium Acetate in Padding Solution

Sample	Conc. of ammonium acetate, %	Tensile strength, Kg./cm.	Elongation, %	Crease resistance, %
Unmodified cotton				
uncured		7.40	10.1	41.0
cured	2.0	6.40	11.8	46.0
Cyanoethylated cotton				
uncured		8.91	13.5	50.0
cured	2.0	6.70	12.0	51.3
Carbamoylethylated cotton				
uncured		8.85	13.0	49.5
cured	0.5	7.48	12.7	50.8
	1.0	7.28	12.2	51.3
	1.5	7.40	12.6	53.5
	2.0	6.95	11.5	54.3

TABLE VI. Effects of Formaldehyde-Curing Temperature on Crease Resistance, Tensile Strength, and Elongation Using Ammonium Acetate Catalyst

Sample	Temp. of cure, °C.	Tensile strength, Kg./cm.	Elongation, %	Crease resistance, %
Unmodified cotton	uncured	7.10	10.1	42.0
Cyanoethylated cotton	uncured	7.80	11.6	49.5
Carbamoylethylated cotton	uncured	7.60	11.2	50.0
	110	7.10	10.2	50.5
	120	7.02	9.7	51.0
	130	6.85	9.6	51.5
	140	6.56	9.2	51.8
	150	6.30	8.8	52.2

It appears that ammonium acetate catalyst is too weak to produce a significant cross link, not only in the unmodified and cyanoethylated cotton but in the carbamoylethylated cotton.

Effects of nitrogen content of cyanoethylated cotton. Three kinds of partially cyanoethylated cotton containing 2.11, 2.73, and 4.44% N (8.86, 11.72, and 20.60 mole % degree of cyanoethylation respectively) were carbamoylethylated for 40 min. at 40° C. and pH 9.1, then formaldehyde-cured at 110–150° C.

using 1.5% secondary ammonium phosphate padding solution. The physical properties are compared in Tables IV and VII.

From these results, it is concluded that the treatment of the cyanoethylated cotton containing about 2.5% N (10 mole % degree of cyanoethylation) is most effective on the improvement of crease resistance. The higher cyanoethylation seems to cause a difficulty in carbamoylethylation because of its hydrophobic property and makes it difficult to produce sufficient cross-linking to restrain its greater plasticity, in spite of the advantage of its higher acid resistance.

Tear strength, flex abrasion, and stiffness. Tear strength, flex abrasion strength, and stiffness of the 2.11% N cyanoethylated cotton fabrics formaldehyde-cured after carbamoylethylation were measured. The carbamoylethylation was done for 40 min. at 40° C. and pH 9.2 and the curing done for 10 min. at 123° C. with 1% secondary ammonium phosphate padding solution. The results are shown in Table VIII in comparison with that of the unmodified, cyanoethylated, or carbamoylethylated cotton fabrics, uncured. All the control samples were treated with boiling water.

Tear strength, flex abrasion strength, and stiffness of the carbamoylethylated cotton fabrics are not depressed so much by the formaldehyde-curing. It is noteworthy that the flex abrasion strength of the carbamoylethylated cotton and the formaldehyde-cured sample are somewhat greater than that of the cyanoethylated cotton.

TABLE VII. Effects of Nitrogen Content of Cyanoethylated Cotton on Crease Resistance, Tensile Strength, and Elongation After Carbamoylethylation and Formaldehyde-Curing

Sample	Temp. of cure, °C.	Tensile strength, Kg./cm.	Elongation, %	Crease resistance, %	Discoloration
Cyanoethylated cotton (2.73% N)	uncured	9.40	13.4	50.0	
Carbamoylethylated cotton (2.61% N)	uncured	9.05	13.0	49.0	
	110	7.54	11.3	54.8	
	120	7.26	11.0	57.0	
	130	7.05	10.4	59.4	
	140	6.92	10.0	61.3	slight yellowish
	150	6.45	9.4	63.8	pale yellow
Cyanoethylated cotton (4.44% N)	uncured	8.64	14.4	46.4	
Carbamoylethylated cotton (4.28% N)	uncured	8.50	14.0	45.4	
	110	7.05	13.0	49.7	
	120	6.84	12.8	51.0	
	130	6.60	12.4	52.4	
	140	6.42	12.1	52.6	slight yellowish
	150	5.90	11.4	52.3	slight yellowish

TABLE VIII. Comparison of Tensile, Tear, and Flex Abrasion Strength, Elongation, Crease Resistance, Stiffness, and Moisture Regain of Unmodified, Cyanoethylated, Carbamoylethylated, and Formaldehyde-Cured Cotton Fabrics Using Secondary Ammonium Phosphate Catalyst

Sample	N, %	Tensile strength, Kg./cm.	Tear strength, Elmendorf's unit	Elongation, %	Crease resistance, %	Flex abrasion strength, No.	Stiffness, L^3W*	Moisture regain,** %
Unmodified cotton		7.62	32.8	10.2	44.9	572	2.07	8.10
Cyanoethylated cotton	2.11	8.24	29.6	12.0	49.4	234	3.36	6.13
Carbamoylethylated cotton	2.07	7.90	23.6	11.0	51.1	319	2.41	6.84
Carbamoylethylated cotton, cured	2.05	6.70	21.5	9.8	60.9	283	2.34	6.39

* L = critical length in cm., W = weight in g./cm.^{2} by Clark's method.
** Moisture regain at 65% RH and 18° C.

Moisture regain. The moisture regain of the cyanoethylated cotton is increased by the carbamoylethylation, but that of the carbamoylethylated cotton is decreased somewhat by the formaldehyde curing, as shown in Table VIII.

Dyeing properties. The cyanoethylated cotton retains the increased affinity for acid and basic dyes after carbamoylethylation or subsequent formaldehyde-curing. Also, the affinity for direct dyes is almost unaffected by the formaldehyde-curing.

Conclusions

Carbamoylethylation of the cotton fabrics was performed by the hydrogen peroxide treatment of partially cyanoethylated cotton without greater oxidation damage. The infrared absorption measurements and the behavior of the fabrics toward formaldehyde appeared to indicate that carbamoylethylation had occurred.

By mild acid-catalyzed formaldehyde-curing, the crease resistance of the carbamoylethylated cotton fabrics was improved above that of the cyanoethylated cotton, indicating some extent of formation of N-methylene amide cross link. After curing, the carbamoylethylated cotton has retained good dyeing properties. Although improvement has not yet been sufficient, the process should be noteworthy as a very simple method of modification of the partially cyanoethylated cotton.

In the following paper (Part II), formaldehyde-curing after amidoximation of the partially cyanoethylated cotton will be reported.

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Part II: Formaldehyde-Curing after Amidoximation

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Abstract

By amidoximation with the aqueous hydroxylamine and subsequent formaldehyde-curing in the presence of a weak acid catalyst such as ammonium acetate or even in the absence of catalyst, the crease resistance of cyanoethylated cotton fabrics containing a low percentage of nitrogen was improved significantly without much loss in the tensile strength and elongation, but a decrease in the flex abrasion and tear strength occurred. From the results, it was deduced that the longer cross link chain might be formed to some extent between adjacent amidoxime or hydroxamic acid groups in different cellulose molecules. After curing, the amidoximates retain great affinities for acid dyes and have a wool-like hand.

Introduction

In the previous publication from our laboratory, it was stated that the crease resistance and dyeing properties of partially cyanoethylated cotton fabrics were improved significantly by amidoximation with aqueous hydroxylamine; amidoximates were given a wool-like hand without much loss in tensile strength, tear strength, and elongation [1]. In the present paper, we attempted further improvement of the crease resistance by means of formaldehyde-curing of the amidoximates.

It has been reported by F. Schouteden that the amidoximation products of powdered polyacrylonitrile in an aqueous dispersion appear to be hydrolyzed into the hydroxamic acid exclusively under certain conditions [2]. The kinetics of the amidoximation of partially cyanoethylated cotton in the aqueous hydroxylamine have not yet been studied. However, we recently observed that the —CN groups amidoximated in the aqueous hydroxylamine were partly hydrolyzed into the hydroxamic acid groups not only in the partially cyanoethylated cotton but in the polyacrylonitrile fiber. The details of the results will be reported at a later date.

Be that as it may, it has been known since 1889 that the amidoxime group, such as in benzamidoxime, reacts with aldehyde to form the condensation product having a 1,2,4-oxadiazole ring [3]. In the condensation reaction with formaldehyde, the methylene amidoxime ring should be formed. In the formaldehyde-curing of partially amidoximated cyanoethyl cellulose cotton, not only the intramolecular but also intermolecular condensation reactions may presumably take place. If so, the methylene group may be introduced as a cross-linker between amide groups, oxime groups, or amide and oxime groups of adjacent amidoxime groups in different cellulose molecules. Also, between hydroxamic acid groups or hydroxamic acid and amidoxime groups, the formation of the analogous cross link may exist. Thus, the formation of the longer chain of cross links and the consequent improvement of the crease resistance–strength relationship are expected.

Experimental

Materials

Partially cyanoethylated cotton fabrics containing 2.1–2.7% nitrogen were used.

Amidoximation

Aqueous 2.29% hydroxylamine hydrochloride solutions, to which were added 0.02% polyethylene oxide lauryl ether as a wetting agent, were used; they were controlled to pH 7.5 with sodium hydroxide solution. Samples rolled in layers with stainless steel wire gauze were reacted hanging in the reaction vessel with a magnetic stirrer. The liquor ratio was 50 : 1. The temperature of the reaction systems was increased from 50° C. or 60° C. to 97–98° C. slowly (20–30 min.) and kept for 10–60 min. at 97–98° C. With water-washing of the reaction products, the discoloration from slight blue to yellowish brown, tending to increase with increase in the degree of amidoximation, appears. Occasionally, in order to prevent the discoloration, acid scouring by 0.3–0.5% hydrochloric acid (20° C., 20 min.) was added to

the washing process, with tolerable success. The nitrogen content of the products was determined by the semimicro Kjeldahl procedure.

Formaldehyde-Curing

The amidoximates of cyanoethylated cotton fabrics were soaked in the aqueous solution containing 12% formaldehyde with or without acid catalyst (secondary ammonium phosphate or ammonium acetate), pressed out to about 100% pickup of the solution, and cured for 10 min. at 110–145° C. The cured samples were washed with hot water until there was no detection of the free formaldehyde. The bound aldehyde was not determined.

Test Procedures

All tests of the mechanical properties were carried out the same as in the previous report.

Discussion and Results

Formaldehyde-Curing Using Secondary Ammonium Phosphate Catalyst

By use of 2.72% N cyanoethylated cotton (11.61 mole % degree of cyanoethylation), the amidoximation was carried out for 15, 30, and 60 min. at 98° C. From the nitrogen contents of 3.61, 3.78, and 4.18% determined, ignoring hydrolysis into hydroxamic groups, calculated mole % degree of amidoximation would be 4.05, 4.86, and 6.80.

The formaldehyde-curing of the amidoximates was done for 10 min. at 110° C. after padding in the formaldehyde solution containing 0.5, 1.0, or 2.0% secondary ammonium phosphate catalyst. After the curing, the discoloration increased. Mechanical properties of the treated fabrics were measured; results are shown in Table I.

Expectedly, it is observed that formaldehyde-curing improves remarkably the crease resistance of the partial amidoximate of cyanoethylated cotton without loss in elongation; however, a considerable loss in tensile strength occurs.

Formaldehyde-Curing Using Ammonium Acetate Catalyst

As the weaker catalyst, ammonium acetate was used. By use of the same 2.7% N cyanoethylated cotton as used above, the amidoximation was carried out for 5, 15, 30, and 60 min. at 98° C. The amidoximates were formaldehyde-cured for 10 min. at 110° C. using 0.5% ammonium acetate padding solution (pH 4.48). The mechanical properties of the cured fabrics are shown in Table II.

It is interesting that the crease resistance of the partial amidoximates of cyanoethylated cotton is improved by curing, to nearly the same extent as in the use of secondary ammonium phosphate catalyst and without as much loss in strength and elongation. The improvement appears to tend to level after 15 min. of amidoximation. On the contrary, the crease resistance of the unmodified or cyanoethylated cotton is not improved by curing. The discoloration after curing was less than that following the use of secondary ammonium phosphate catalyst.

Next, partially cyanoethylated cotton containing 2.11% N (8.86 mole % degree of cyanoethylation) was amidoximated for 10 min. at 98° C. In the

TABLE I. Effects of Formaldehyde-Curing on Crease Resistance, Tensile Strength, and Elongation Using Secondary Ammonium Phosphate Catalyst

Time of amidoximation, min.	Content of nitrogen, %	Conc. of $(NH_4)_2HPO_4$, %	Tensile strength, Kg./cm.	Elongation, %	Crease resistance, %
Unmodified cotton		uncured	8.02	8.3	47.2
Cyanoethylated cotton	2.72	uncured	9.34	11.6	53.1
Amidoximate of cyanoethylated cotton					
15	3.61	uncured	6.17	11.2	69.0
		2.0 (pH 2.7)	3.60	12.0	80.9
30	3.78	uncured	6.10	10.8	67.8
		1.0 (pH 3.0)	3.82	10.0	89.6
60	4.18	uncured	5.96	11.8	68.3
		0.5 (pH 3.1)	3.86	13.4	90.9

washing process of the reaction products, 0.3% hydrochloric acid scouring was done, resulting in hardly any discoloration. The amidoximates were formaldehyde-cured for 10 min. at 110°, 120°, 130° and 145° C. using 0.5% ammonium acetate padding solution (pH 4.30). The increase of discoloration by the curing was slight except in the case of the 145° C. cure. Mechanical properties of the cured fabrics are shown in Table III. Improvement of the crease resistance seems to tend to level above 130° C. cure.

TABLE II. Effects of Formaldehyde-Curing on Crease Resistance, Tensile Strength, and Elongation Using Ammonium Acetate Catalyst

Time of amidoximation, min.	Content of nitrogen, %	Cured or uncured	Tensile strength, Kg./cm.	Elongation, %	Crease resistance, %	Discoloration
Unmodified cotton						
		uncured	7.28	9.4	46.5	none
		cured	6.88	13.4	43.3	none
Cyanoethylated cotton						
	2.72	uncured	8.52	12.2	57.8	none
		cured	7.68	14.8	54.3	none
Amidoximate of cyanoethylated cotton						
5	3.18	uncured	7.12	11.0	69.5	hardly any
		cured	6.54	10.2	73.0	slight yellowish
15	3.66	uncured	7.18	11.4	68.3	yellowish blue
		cured	6.38	11.4	80.8	pale yellow
30	3.58	uncured	6.58	11.2	72.8	yellowish blue
		cured	5.40	9.8	80.5	pale yellow
60	4.26	uncured	5.78	11.5	66.0	yellowish brown
		cured	5.16	10.0	81.8	pale brown

TABLE III. Effects of Curing in the Presence or Absence of Formaldehyde, with Ammonium Acetate Catalyst at Varying Temperature of Cure on Crease Resistance, Tensile Strength, and Elongation

Sample	Content of nitrogen, %	Temp. of cure, ° C.	Tensile strength, Kg./cm.	Elongation, %	Crease resistance, %	Discoloration
Unmodified cotton		uncured	7.24	10.2	43.0	none
Cyanoethylated cotton	2.11	uncured	8.30	11.4	50.2	none
Amidoximate of cyanoethylated cotton						
washed with water	2.64	uncured	7.30	10.8	56.3	slight yellowish
washed with 0.3% HCl	2.58	uncured	6.98	10.6	56.0	hardly any
		cured with $CH_2O—CH_3COONH_4$				
		110	5.14	10.2	85.0	hardly any
		120	4.62	9.6	84.5	hardly any
		130	4.20	9.5	88.8	hardly any
		145	3.60	9.6	86.0	slight yellowish
		cured with CH_3COONH_4				
		110	6.42	10.2	55.8	hardly any
		120	6.22	10.0	56.3	hardly any
		130	6.04	9.8	56.0	hardly any
		145	5.68	9.6	58.3	slight yellowish

Curing in the Absence of Formaldehyde

In order to know the action of formaldehyde in the curing, the non-formaldehyde curing was done with the use of ammonium acetate only. The results are shown in Table III. It can be seen that crease resistance is not improved at all.

Since ammonium acetate catalyst is too weak to introduce the formal cross-linkage between the non-cyanoethylated —OH groups, as observed in Table II and the previous report, the improvement in crease resistance of the formaldehyde-cured amidoximate should be attributed to any cross-linking caused by the condensation reaction between formaldehyde and amidoxime or hydroxamic acid groups.

Non-Catalyzed Formaldehyde-Curing

Compared with results obtained in the previous report, it is noteworthy that amidoxime or hydroxamic acid groups are more readily cross-linked than carbamoyl groups with formaldehyde. Therefore, formaldehyde-curing was tried in the absence of acid catalyst at varying temperatures of cure (90–130° C.). With 2.70% N cyanoethylated cotton, the amidoximation was done for 15 min. at 98° C. The products were scoured with 0.5% hydrochloric acid, giving 3.50% N and hardly any discoloration. The mechanical properties of the cured amidoximates are shown in Table IV and Figures 1, 2, and 3, compared with those of the acid-catalyzed formaldehyde-cured

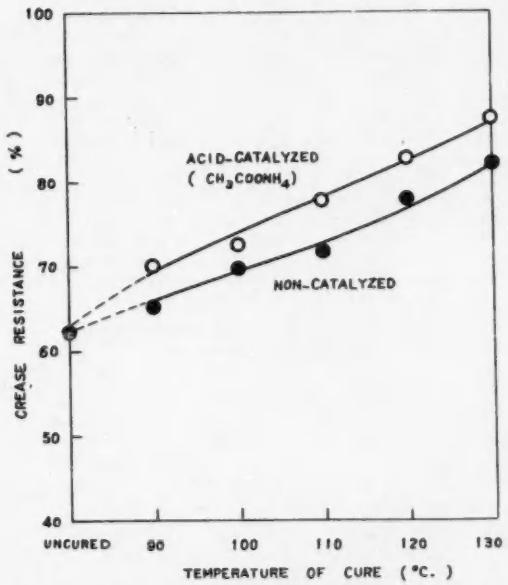

Fig. 1. Effect of formaldehyde-curing in the presence or absence of ammonium acetate catalyst at varying temperatures of cure on crease resistance of the amidoximate of partially cyanoethylated cotton fabrics.

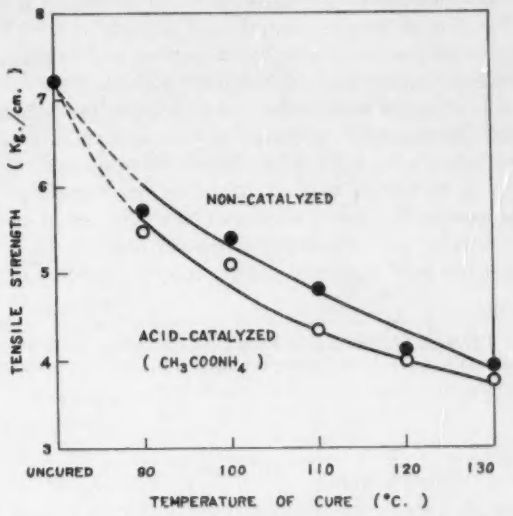

Fig. 2. Effect of formaldehyde-curing in the presence or absence of ammonium acetate catalyst at varying temperatures of cure on tensile strength of the amidoximate of partially cyanoethylated cotton fabrics.

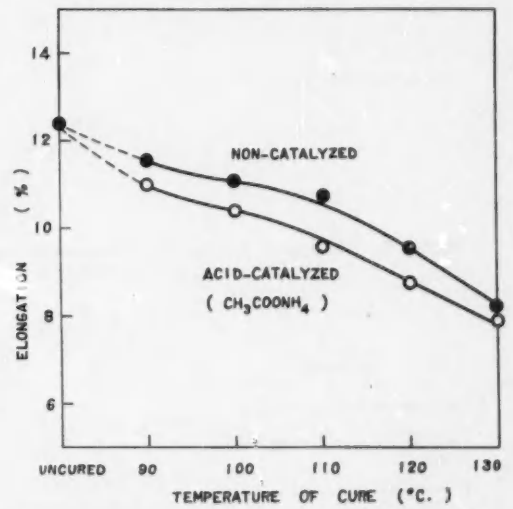

Fig. 3. Effect of formaldehyde-curing in the presence or absence of ammonium acetate catalyst at varying temperatures of cure on elongation of the amidoximate of partially cyanoethylated cotton fabrics.

fabrics using 0.5% ammonium acetate padding solution (pH 4.35).

In both acid-catalyzed and non-catalyzed formaldehyde-curing, it is observed that crease resistance increases with increasing cure temperature in the range of 90–130° C., accompanied by a corresponding loss of tensile strength and elongation. It is interesting that, even in the absence of acid catalyst, crease resistance is considerably improved, though somewhat less than in the presence of catalyst. Since the formaldehyde padding solution used here was slightly acidic (pH 4.0) because of a commercial grade formaline used, it might act as a catalyst; however, the aspects obtained above will not be inconsistent with Tiemann's report, in which no catalyst has been employed for the reaction of benzamidoxime with aldehyde [3]. Also, a catalytic action of hydroxamic acid groups which are found to coexist to some extent with amidoxime groups may be concerned.

Tear Strength, Flex Abrasion Strength, and Stiffness

Tear strength, flex abrasion strength, and stiffness of the fabrics formaldehyde-cured after amidoximation of 2.1% N cyanoethylated cotton were measured. The amidoximation was done for 20 min. at 97° C. and the curing for 10 min. at 110–118° C. with 0.5% ammonium acetate padding solution (pH 4.40). The results are shown in Table V in comparison with that of the unmodified, cyanoethylated, or amidoximated cotton, uncured.

TABLE IV. Effects of Formaldehyde-Curing in the Presence or Absence of Ammonium Acetate Catalyst at Varying Temperature of Cure on Crease Resistance, Tensile Strength, and Elongation

Sample	Temp. of cure, °C.	Tensile strength, Kg./cm.	Elongation, %	Crease resistance, %	Discoloration
Unmodified cotton	uncured	7.14	9.6	45.3	none
Cyanoethylated cotton	uncured	8.64	13.8	53.6	none
Amidoximate of cyanoethylated cotton acid-catalyzed	uncured	7.21	12.4	62.0	hardly any
	90	5.46	11.0	70.0	hardly any
	100	5.10	10.4	72.4	hardly any
	110	4.36	9.6	77.8	hardly any
	120	4.02	8.8	83.0	hardly any
	130	3.80	7.9	87.5	slight yellowish
non-catalyzed					
	90	5.72	11.6	65.0	hardly any
	100	5.41	11.1	69.8	hardly any
	110	4.82	10.8	71.6	hardly any
	120	4.10	9.6	78.0	hardly any
	130	3.94	8.2	82.0	slight yellowish

TABLE V. Changes of Tear and Flex Abrasion Strength, Stiffness, and Moisture Regain by Cyanoethylation, Amidoximation, and Formaldehyde-Curing of Partially Cyanoethylated Cotton

Sample	Nitrogen content, %	Tear strength, Elmendorf's unit	Flex abrasion strength, No.	Stiffness, L^3W	Moisture regain (RH 65%), %
Unmodified cotton		34.9	358	2.10	7.65
Unmodified cotton boiled with water		45.6	675	2.02	8.18
Cyanoethylated cotton boiled with water	2.10	29.0	272	2.16	6.77
Amidoximate of cyanoethylated cotton	2.71	22.3	349	1.86	7.38
Formaldehyde-cured amidoximate	2.66	15.2	174	1.98	7.46

It is seen that a considerable decrease of tear and flex abrasion strength has occurred in the cured amidoximate; however, the lower stiffness has been retained to a fairly good extent, corresponding with a wool-like hand.

Moisture Regain

The moisture regain (65% RH, 11° C.) of partially cyanoethylated cotton was increased by the amidoximation and almost unaffected by the subsequent formaldehyde-curing, as shown in Table V.

Discoloration

Discoloration of the amidoximates was prevented to a certain degree by scouring with about 0.5% hydrochloric acid in the washing process immediately after hydroxylamine treatment. This virtue has been retained tolerably after the formaldehyde-curing. Such a degree of discoloration was undesirable for undyed cotton, but was not obstructive to most dyeing.

Dyeing Properties

The amidoximate of partially cyanoethylated cotton has retained increased affinities for various acid dyes after formaldehyde-curing. The affinities for "Eosine" and basic dyes, decreased by the amidoximation, could not be recovered after curing. Also, affinities for direct dyes were almost unaffected by curing.

Conclusions

By acid-catalyzed or non-catalyzed formaldehyde-curing, crease resistance of the amidoximates of partially cyanoethylated cotton fabrics was improved significantly without much loss in tensile strength and elongation; the great affinities for acid dyes were retained.

From the results, it was deduced that intermolecular cross links between amidoxime or hydroxamic acid groups might be formed.

Further work is in progress dealing with the reactions between formaldehyde and amidoxime or hydroxamic acid groups.

Acknowledgment

The authors are indebted to the Japan Cotton Technical Institute, Osaka, for their financial assistance. We are also grateful to Professor W. Tsuji and Dr. R. Kitamaru of the Institute for Chemical Research, Kyoto University, for preparing partially cyanoethylated cotton fabrics for us.

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Observations on the Use of Copper Formate as a Rotproofer for Cotton Fabric

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Introduction

Of the various organic compounds of copper which have been investigated for possible use as fungicides, the copper salts of the lower molecular weight fatty acids have not received much attention. The only exception is the acetate, which has been used in reactions involving the deposition of copper by double decomposition reaction. This limited use of these compounds as fungicides *per se* has been undoubtedly due to their relatively high solubility in water which renders them readily removable in weathering. However, recent work by Abrams and Bottoms [1] on the use of copper formate serves as a reminder that this compound on heating at low to moderate temperatures undergoes a type of decomposition different from that suffered by the other fatty acid salts of copper or by a number of other organic copper compounds investigated by those authors.

Mechanism of Thermal Decomposition of Cupric Formate

The mechanism of the thermal decomposition of cupric formate *in vitro* has been studied by a number of investigators. Kohlschütter and Christen [7] studied the process at 200° C. *in vacuo* and concluded that two types of breakdown were involved, these being generally as follows:

$$\mathrm{Cu(HCOO)_2} \begin{cases} \nearrow \mathrm{Cu + H_2 + 2CO_2} \\ \searrow \mathrm{CuCO_3 + H_2 + CO} \end{cases} \qquad (1)$$

These authors claim that the course of the reactions, admittedly complex, is influenced by the crystal form of the formate used and that the tendency of the gaseous reaction products to react with the solid products introduces a further complication.

The formation, in the reaction, of metallic copper (or at least of some substance capable of producing a copper-colored mirror on glass) is the basis of a patent by Marboe [10] covering the formation of copper mirrors on glass by volatilizing metal formates in a vacuum chamber at 350–400° F. This reference to volatilization is in line with earlier work by Korosky [9], who refers to the production of a volatile compound of copper on heating cupric formate. This author states that this volatile compound readily decomposes to give elementary copper which deposits as a mirror on nearby glass surfaces. Experiments, claimed to prove the existence of the volatile copper compound, are described, but later Keller and Korosky[6] came to the conclusion that in his earlier work, Korosky had been dealing with an extremely fine aerosol containing cuprous formate, which readily decomposes to metallic copper. They conclude that the main reaction involved is

$$\mathrm{Cu(HCOO)_2 \rightarrow Cu + HCOOH + CO_2}$$

and that minor amounts of the copper are formed by the reactions

$$\mathrm{2Cu(HCOO)_2 \rightarrow 2CuHCOO + HCOOH + CO_2}$$

or

$$\mathrm{2Cu(HCOO) \rightarrow 2CuHCOO + H_2O + CO + CO_2}$$

and

$$\mathrm{2CuHCOO \rightarrow 2Cu + H_2 + 2CO_2}$$

Bécue [2] studied the thermal decomposition of anhydrous cupric formate prepared from cupric formate tetrahydrate and concluded that there was no evidence of the formation of a volatile compound; he appears to favor Reaction 1 above. Incidentally, this investigator states that the tetrahydrate represents the most common form of the salt. He also studied the decomposition of basic cupric formate to which the formula $\mathrm{Cu(HCOO)_2 \cdot 2\,Cu(OH)_2}$ was assigned by Riban [11] and the one having the formula $\mathrm{Cu(HCOO)_2 \cdot 3\,Cu(OH)_2}$ as described by Fowles [5]. Both of these compounds decomposed in glass to give a copper mirror, the data suggesting the following reactions:

$$Cu(HCOO)_2 \cdot 2Cu(OH)_2 \rightarrow 2CO_2 + 3H_2O + 2Cu + CuO$$

and

$$Cu(HCOO)_2 \cdot 3Cu(OH)_2 \rightarrow 2CO_2 + 4H_2O + 2Cu + 2CuO$$

In a study of the kinetics of the thermal decomposition of metallic formates, Kornienko [8] found that the main products of the reaction were a metal oxide and products of the decomposition of formic acid; where free metal was present in the reaction products it could be attributed to the reduction of the oxides by the gaseous decomposition products, notably carbon monoxide and hydrogen. It is of interest to note that the mechanism postulated by this author would make it possible for cuprous oxide to be one of the reaction products.

From the above it would appear that, on heating *in vitro*, cupric formate undergoes a complex type of breakdown to give copper oxides and free copper. Moreover, the color of the residue on heating the formate suggests that the oxide present is probably cuprous oxide.

Decomposition of Cupric Formate on Cotton Cellulose and the Properties of the Treated Cotton

In the process described by Abrams and Bottoms [1], cotton is treated with an aqueous solution of cupric formate, dried, and then heated to around 120° C. in an air oven or, preferably, in an autoclave. The duration of heating recommended by these authors is not critical and depends largely on the type of cellulosic material undergoing treatment, it being only necessary to heat for a period sufficient to produce the decomposition of the formate, as judged by the characteristic color change to a brown color, later changing to olive green, where dry heat (e.g., an oven) is used, or to a tan or light olive color in the case of steam autoclaving.

The above-mentioned authors claim that cotton cellulose treated in this way shows evidence of having undergone cross-linkage, which they claim to be through the medium of the copper, to give a product which is insoluble in cuprammonium hydroxide or cupriethylenediamine and which cannot be xanthated. Moreover, it is claimed that the copper is only partially removed from the cotton by leaching in aqueous ammonia. The amount of copper held by the cellulose appeared to be proportional to the degree of crystallinity of the cellulose, with viscose rayon (low crystallinity) retaining 90.5% of the copper originally present and ramie (high crystallinity) retaining none. In the case of cotton and rayon the treatment produces a high degree of resistance to microbiological attack.

In the course of work in which we examined the Abrams and Bottoms treatment on cotton, we were unable to duplicate their data, especially with reference to those properties which are claimed to relate to the cross-linking of the cellulose through the medium of the copper. Thus, for example, all of our samples were freely dispersible in cuprammonium hydroxide reagent having the composition 15.0 ± 0.1 g./l. copper and 200 ± 10 g./l. ammonia as normally employed in carrying out fluidity measurements on textile cellulose. The copper present in our samples was readily removable by a series of aqueous ammonia rinses or on exposure to weathering outdoors. In addition, we did not find the resistance to microbiological attack of the treated cotton to be greater than would be expected for fabrics containing the same level of copper in the form of cuprous oxide.

Materials and Methods

Cotton Duck

Unbleached army duck weighing 11.7 oz./sq. yd. was used.

Copper Formate

Copper carbonate was dissolved in dilute formic acid, the powder being mixed into a thin suspension with water and just enough of the acid added to effect solution. The solution was then allowed to evaporate to dryness at room temperature. It was found that the solid residue showed evidence of having undergone some basic compound formation, since on being stirred in water, it did not dissolve completely but gave a pale blue residue which, however, readily dissolved on adding a small amount of formic acid and heating. The solutions used in the treatment of our samples were prepared in this way and thus contained a small amount of free acid.

Treatment

Strips of the duck 6×18 in. with the short dimension in the direction of the warp were wetted out in 0.05% Aerosol OT solution, rinsed, squeezed to remove excess water, and immersed in the treating bath of copper formate containing approximately 1.5 or 0.75% copper for 15 min. at room temperature; the pH of the solution was 4.86. The samples

TABLE I. Breaking Strength Loss and Increase in Fluidity Data for Samples Treated with Copper Formate

Sample	Method of heating	Initial copper content, %	BSL %	ΔF, rhes
A	Oven	0.78	37	17.5
B	Oven	0.43	15	9.5
C	Autoclave	0.77	12	1.3
D	Autoclave	0.43	8	2.1

TABLE II. Effect of Oven Heating on BSL, ΔF and Copper Number of Untreated and Treated Unbleached Cotton Duck

Sample	Time of heating, hr.	BSL %	ΔF, rhes	Copper number
Untreated	7½	9	2.6	0.83
Untreated	24	16	4.2	0.83
Untreated	48	20	5.8	0.83
Untreated	96	25	7.6	0.98
Untreated	192	28	8.4	1.03
Treated with copper formate to contain 0.87% copper	18–24	17	8.4	1.42

were then put through squeeze rolls between blotting paper and dried at room temperature. When dry, they were of a light to medium greenish-blue color.

Oven heating. Half of the samples for each concentration of copper were placed in a constant temperature oven at 120° C. until a change to a brownish color took place. This required approximately 24 hr. On standing in the air the samples became olive-green.

Autoclaving. The other half of the samples were heated in an autoclave at 120° C. and 15 lb./sq. in. gauge pressure for ¾ hr. The color changed from the original greenish-blue to a yellowish tan.

Water Leaching

The samples were leached in running water at 24±3° C. for 24 hr.

Ammonia Leaching

Treated fabric (100 g.) was placed in 3 l. of 4% ammonium hydroxide for 2 hr. and frequently stirred. This was followed by washing in running tap water. This cycle was repeated until no more color was observed in the ammonia solution after being in contact with the sample for 2 hr. This procedure is the same as that used by Abrams and Bottoms [1] who do not, however, specify the fabric : liquor ratio used.

Outdoor Exposure

Strips of the treated fabrics were exposed for 4 months (June–September) on the roof of the Applied Chemistry Building, National Research Council, Ottawa. The samples were held at an angle of 45° facing south. Two 6×18 in. strips were exposed for each sample, one of these being used to determine breaking strength loss, increase in fluidity, and loss of metal and the other being used to measure the effect of weathering on resistance to microbiological attack, as judged by the breaking strength loss occurring in two-week soil burial.

Soil Burial

This was carried out according to Method 28, Procedures 28B and 28D, of Schedule 4-GP-2, "Methods of Testing Textiles," of the Canadian Government Specifications Board, National Research Council, Ottawa.

Breaking Strength

This was the usual 1-in. raveled-strip test carried out according to Method 9A2(a) of the above Schedule. The samples were broken on a Scott pendulum-type machine operating at a pulling speed of 12 in./min., the initial separation of the jaws being 3 in. and machine capacity 0–150 lb.

Cuprammonium Fluidity

This was carried out according to Method 17 of the above Schedule. The cuprammonium solution used is the one described by Clibbens and Little [3] and contains 15.0±0.1 g./l. copper and 200±10 g./l. ammonia (NH_3).

Copper Analysis

This was carried out as described previously [12].

Data

Extent of Degradation of Cotton During Treatment

Samples of duck treated as above were examined for breaking strength loss (BSL). It was found that there was appreciable BSL, this being higher for the oven-treated sample. This raised the question of the basis on which the BSL's should be calculated; it was decided to use the breaking strength

of the untreated duck which had been thoroughly soaked in water and allowed to remain wet for several hours in order to stabilize the fabric with respect to shrinkage. Since the treated samples appeared to be freely dispersible in cuprammonium hydroxide, measurements of increase in fluidity (ΔF) were also carried out.

The data are given in Table I, where it will be seen that, for the samples having the higher content of copper, oven-heating caused a BSL of 37% and autoclave-heating 12%, the corresponding ΔF's being 17.5 and 1.3 rhes. The samples having the lower copper content showed lower BSL's and ΔF's. These data suggest that heating in the presence of air leads to considerable chemical degradation; this may be due to one or more of the following: oxidative attack, oxidative attack enhanced by the catalytic effect of the copper or cuprous oxide present, or hydrolytic attack resulting from the action of formic acid released during heating.

In an attempt to separate some of these effects, a series of experiments was carried out in which samples of unbleached, untreated duck were heated in the oven at 120° C. for various periods of time, the BSL's and ΔF's being measured after heating. In addition, the copper numbers of the heated samples were determined by the Heyes' micro adaptation of the Schwalbe-Braidy method [4]. The data, compared with those obtained with a sample of formate-treated duck (0.87% copper) heated at 120° C. until the required color change occurred, are given in Table II. It will be noted that the copper numbers rise slowly with increased time of heating although the copper number of the sample heated for 192 hr. (1.03) is not as great as that of the heated copper formate-treated sample (1.42) which had been heated for only 18–24 hr., indicating the effect of some other factor tending to increase the copper number.

In order to investigate the effect of hydrolytic treatment, samples of the unbleached duck which had been well wetted-out in water and squeezed between blotters were immersed in aqueous sulfuric acid (354 ml. conc. acid to 1448 ml. water) at room temperature for progressively increasing periods, with frequent shaking, followed by thorough washing and neutralization of any residual acid with dilute ammonia and further washing. Measurements of BSL, ΔF, and copper number were then made on the dried

TABLE III. Effect of Steeping Unbleached Duck in Dilute Sulfuric Acid

Time of immersion in acid, hr.	BSL, %	ΔF, rhes	Copper number
0.75	8	3.7	0.40
2.75	25	9.8	0.94
5.5	35	12.5	1.18
16	59	23.0	1.90
28.5	65	24.4	2.03
48	77	30.4	3.44

TABLE IV. Removal of Copper from Treated Samples by Leaching in Ammonium Hydroxide and by Water

Treatment	High-copper samples		Low-copper samples	
	Copper content, %	Copper remaining, %	Copper content, %	Copper remaining, %
(a) Impregnation with copper formate solution only	0.78	—	0.43	—
(b) Treated fabric from (a) heated in oven	0.78	100	0.43	100
(c) Treated fabric from (b) water rinsed	0.57	73	0.33	77
(d) Treated fabric from (b) ammonia rinsed	0.32	41	0.21	49
(e) Treated fabric from (a) heated in autoclave	0.77	100	0.43	100
(f) Treated fabric from (e) water rinsed	0.74	96	0.38	88
(g) Treated fabric from (e) ammonia rinsed	0.34	44	0.24	56

and conditioned samples. The data, given in Table III, show that the copper number increases much more quickly with time than with the oven-heated samples. In the formate-treated oven-heated samples showing damage the BSL was 17% and the copper number 1.42, whereas for the unbleached, untreated duck, the copper numbers for the heat-damaged and acid-damaged samples showing 17% BSL were 0.83 and 0.70 respectively. This suggests that the damage shown on heating the treated sample was probably a mixture of oxidative (heat) and hydrolytic (acid) damage.

Extent to which the Copper is Retained by the Treated Samples

Effect of leaching with ammonium hydroxide. Portions of the samples listed in Table I were given an ammonia leaching treatment as described above. The copper contents of the samples were then determined; data are given in Table IV. The results are generally similar to those obtained by Abrams and Bottoms. The percentage of copper retained after water leaching (c) and (f) was greater in the autoclaved samples.

It was considered that this incomplete removal of copper may be due to the fact that copper trapped within the fibers is being held by the fabric and that this may migrate to the surface of the fiber during drying, thus being susceptible to removal in a subsequent ammonia rinse. This was found to be the case. Samples of treated fabrics were given two or three ammonia leaches, without intermediate drying, depending upon the amount of blue color finally observed in the solution, dried, and analyzed for copper. This process was then repeated, two or three rinses being carried out at a time, with intermediate drying between each lot of two or three rinses until a total of twelve rinses and five dryings had been carried out. The data, given in Table V, show that the greater part of the copper is removed by the ammonia leaching where the samples are subjected to intermittent drying.

Finally, cupric formate solution was applied to a fabric made from an inert nonswelling fiber (*viz.* glass) of approximately the same weight and construction as the cotton duck used in this work; the fabric was heated as above. The color changes occurring on oven- and autoclave-heating were similar to those shown by the cotton, but of less intensity, this being doubtless due to the lower pick-up of solution and hence the lower content of copper. It was found that approximately 99% of the copper was removed by two rinses in the case of the oven-heated and 96% for the autoclave-heated samples. Here, the amount of migration likely to occur would be considerably less than in the cotton fabric used above, the accessibility of the copper to the ammonia being vastly greater than with the treated cotton.

Effect of outdoor weathering. The effect of outdoor weathering on the retention of copper by treated fabrics containing high and low levels of copper is shown in Table VI, the effect on the content of residual copper by the method of treatment being indicated. It will be seen that weathering results in

TABLE V. Retention of Copper by Treated Duck Subjected to Repeated Ammonia Leaching with Intermediate Drying

Leaching treatment	Oven heated duck			Autoclaved duck		
	Copper content, %	Copper remaining, %	Fluidity, rhes	Copper content, %	Copper remaining, %	Fluidity, rhes
None	0.87	—	11.5	0.73	—	4.4
2 Leachings, then dried	0.33	37.9	—	0.37	50.7	—
5 Leachings, then dried	0.16	18.4	—	0.19	26.0	—
8 Leachings, then dried	0.12	13.8	—	0.10	13.7	—
10 Leachings, then dried	0.072	8.3	—	0.072	9.9	—
12 Leachings, then dried	0.068	7.8	12.5	0.054	7.4	4.7

the practically complete loss of copper from the samples.

While the mechanism of the removal, in weathering, of a copper compound applied to cotton fabric is not clearly understood, all of the copper compounds previously examined have been found [12, 13] to undergo almost complete loss of the copper when weathered outdoors for four months in the

TABLE VI. Loss of Copper by Treated Duck Exposed to Weathering Outdoors

Treatment	High-copper samples		Low-copper samples	
	Initial copper content, %	Loss of copper due to weathering, %	Initial copper content, %	Loss of copper due to weathering, %
(a) Treated with copper formate and oven heated	0.78	99+	0.43	99+
(b) As in (a) and rinsed with water	0.57	—	0.33	—
(c) As in (a) and rinsed with ammonia	0.32	99+	0.21	99+
(d) Treated with copper formate and autoclave heated	0.77	95	0.43	98
(e) As in (d) and rinsed with water	0.74	—	0.38	—
(f) As in (d) and rinsed with ammonia	0.34	99	0.24	99+

TABLE VII. Resistance of Treated Duck to Soil Burial Before and After Outdoor Weathering

Treatment	High-copper samples							Low-copper samples						
		Breaking strength losses, %*							Breaking strength losses, %					
		Before weathering			After weathering				Before weathering			After weathering		
	Initial copper content, %	Due to T	Due to T +B	Due to B	Due to T +W	Due to T +W +B	Due to B (by difference)	Initial copper content, %	Due to T	Due to T +B	Due to B	Due to T +W	Due to T +W +B	Due to B (by difference)
None	—	0	100	100	45	86	41	—	—	—	—	—	—	—
(a) Treated with copper formate and oven heated	0.78	37	37	0	54	79	25	0.43	15	21	6	51	67	16
(b) As in (a) and rinsed with water	0.57	37	25	0	—	—	—	0.33	15	28	13	—	—	—
(c) As in (a) and rinsed with ammonia	0.32	37	25	0	54	78	24	0.21	15	32	17	51	71	20
(d) Treated with copper formate and autocalve heated	0.77	12	2	0	36	48	12	0.43	8	18	10	28	56	28
(e) As in (d) and rinsed with water	0.74	12	2	0	—	—	—	0.38	8	12	4	—	—	—
(f) As in (d) and rinsed with ammonia	0.34	12	10	0	26	74	48	0.24	8	8	0	28	70	42

* All breaking strength losses are based on the strength of the original untreated duck which had been stabilized with respect to shrinkage by prolonged wetting. T = Treatment; B = Burial; W = Weathering.

summer. The data show that the formate treatment behaves similarly.

Fungicidal Efficacy of the Treatment

Samples containing 0.78% and 0.43% of copper as cupric formate were subjected to a two-week soil burial test before and after outdoor weathering for four months. Prior to testing, the samples were subjected to one or other of the various aftertreatments shown in the first column of Table VII, which also gives the data obtained on the fungicidal efficacy of the copper formate treatment.

It will be seen that the high-copper samples as first prepared all showed complete resistance to microbiological attack; in the low-copper samples there was some indication that the autoclave-heated samples were slightly more resistant than the oven-heated ones. After weathering, the samples still showed considerable resistance, although there had been substantially complete loss of copper. This so-called residual effect has been frequently observed with other textile fungicides and is explainable, in part at least, by the resistance to microbiological attack shown by cellulose which has undergone some chemical breakdown to form oxy- or hydrocellulose.

Extent of Actinic Degradation of the Treated Samples on Weathering

This was measured by breaking strength loss and increase in fluidity occurring during exposure outdoors; data are shown in Table VIII. It will be noted that the method of heating used in the treatment seems to have a direct bearing on the loss of strength which takes place during weathering; e.g., for the high-copper oven-heated sample there was the usual comparatively large BSL due to the treatment alone (37%) which was increased to 54% on weathering. In the case of the autoclave-heated sample the initial BSL was much lower (12%); it was increased on subsequent weathering to 36%, the weathering process thus contributing 24%, i.e., somewhat more than in the case of the oven-heated sample. This trend is also observed in the fluidity data. This effect is undoubtedly due to the fact that the autoclaved samples are initially less damaged than the oven-heated ones and thus more susceptible to subsequent breakdown during oxidation.

In the present series of tests it will be noted that the general effect of the copper was one of protection when comparison is made with the BSL and increase in fluidity values shown by the untreated control.

TABLE VIII. Actinic Degradation of Treated Duck Exposed to Weathering Outdoors

Treatment	High-copper samples							Low-copper samples						
		Breaking strength loss, %*			Increase in fluidity, rhes				Breaking strength loss, %			Increase in fluidity, rhes		
	Initial copper content, %	Due to T	Due to T +W	Due to W	Due to T	Due to T +W	Due to W	Initial copper content, %	Due to T	Due to T +W	Due to W	Due to T	Due to T +W	Due to W
None	—	—	—	45	—	—	17.1	—	—	—	45	—	—	17.1
(a) Treated with copper formate and oven heated	0.78	37	54	17	17.5	27.2	9.7	0.43	15	51	36	9.5	24.2	14.7
(b) As in (a) and rinsed with water	0.57	37	—	—	—	—	—	0.33	15	—	—	—	—	—
(c) As in (a) and rinsed with ammonia	0.32	37	54	17	12.3	23.9	11.6	0.21	15	51	36	9.0	23.1	14.1
(d) Treated with copper formate and autoclave heated	0.77	12	36	24	1.3	17.7	16.4	0.43	8	28	20	2.1	15.9	13.8
(e) As in (d) and rinsed with water	0.74	12	—	—	—	—	—	0.38	8	—	—	—	—	—
(f) As in (d) and rinsed with ammonia	0.34	12	26	14	0.8	16.1	15.3	0.24	8	28	20	1.3	13.9	12.6

* T = Treatment; W = Weathering.

Condition of the Copper in the Treated Samples

As has been pointed out in the survey of literature on the thermal decomposition of cupric formate given above, it is considered by some investigators that cuprous oxide is one of the thermal decomposition products of cupric formate. Abrams and Bottoms [1] state that "the orange-red powder that resulted from the autoclaving of copper formate was cuprous oxide." The x-ray diffraction data which they present show the characteristic Cu_2O pattern both in mechanical mixtures of untreated cotton ball-milled with cuprous oxide and in copper formate treated cotton. Abrams and Bottoms, nevertheless, reject the view that the packing of the fine structure of the cellulose with cuprous oxide is responsible for the resistance to microbiological attack shown by copper formate treated samples, giving as their reasons their beliefs that the resistance to leaching by ammonium hydroxide is greatly superior to that which would be shown by a mechanical mixture of cuprous oxide and cotton and that cuprous oxide is not an effective fungicide.

It is believed that the properties of cupric formate treated cotton are in accord with those which might be expected with cotton fabric containing cuprous oxide, this view being supported by the known behavior of cupric formate on heating.

In order to examine the fungicidal properties of cuprous oxide, the resistance to microbiological attack of the following samples was determined as judged visually after exposure to the action of the cellulolytic fungus *Chaetomium globosum* and by loss of breaking strength after a two-week soil burial test.

1. Unbleached, untreated duck (control).
2. Unbleached duck which had been well wetted out in hot water and then immersed in a glucose–Fehling's Solution mixture which was heated so as to obtain precipitation of cuprous oxide in the solution, some of the oxide being picked up mechanically by the fabric.
3. Unbleached duck treated with cupric formate but not heated.
4. Unbleached duck which had been treated with dilute sulfuric acid, as described above, to produce hydrocellulose, followed by heating in Fehling's Solution to give a coating of closely-adhering cuprous oxide on the surface of the fabric.

The data are give in Table IX. It will be seen that Treatment 2, containing a relatively low level of copper in the form of cuprous oxide, nevertheless showed only minor breaking strength loss in the burial test and only very slight growth of *Chaetomium* without noticeable loss in strength in the pure culture test; i.e., it appeared to have substantial resistance to microbiological attack. Sample 4, containing a high level of copper, showed complete resistance to microbiological attack. It is well known that chemical modification of cellulose increases its resistance to microbiological attack. In the present instance the extent of this resistance was determined by subjecting a portion of Sample 4 to soil burial *before* treating with Fehling's Solution, together with a sample of undamaged, unbleached duck. In 5 days' burial the sample containing hydrocellulose lost 24% of its strength and the control 63%. From this it is obvious that in a two-week burial period the hydrocellulose-containing sample would have lost most, but probably not all, of its strength, whereas the control would have been completely disintegrated. Hence the resistance to microbiological attack shown by the hydrocellulose-containing sample with cuprous oxide deposited on it can be attributed only to a minor extent to the presence of the hydrocellulose.

Sample 3, likewise, showed complete resistance, this observation being contrary to the data of Abrams and Bottoms who reported (see their Table IV) that cotton fabric treated with copper formate, at 20° C., to contain 0.75% copper and not heated, supported a heavy growth of *Chaetomium globosum*.

Finally, we considered it of interest to compare the removal of copper by alternate ammonia leaching and drying, following the procedure described above;

TABLE IX. Fungicidal Efficacy of Cuprous Oxide on Cotton Duck

Sample	Copper, %	Breaking strength loss after 2-week soil burial, %	Visual effect in pure culture test, *Chaetomium globosum*
1	None	100	Very heavy growth with disintegration of yarns
2	0.26	13	Very slight growth and no evidence of disintegration
3	0.87	0	Very slight growth and no evidence of disintegration
4	1.22	0	No visible growth

this was carried out on Samples 2 and 4, the data obtained being given in Table X. The data show that the rate of removal of the copper is substantially the same as with cupric formate treated cotton duck. This becomes more obvious when the data for percentage loss of copper vs. number of rinses are plotted (see Figure 1) for the two high-copper samples, i.e., Samples 4 and the autoclave-heated cupric formate treated sample from Table V.

Conclusions

The process involving the heating of cotton fabric impregnated with cupric formate solution to provide a copper content of 0.4% or greater gives a treated fabric having considerable resistance to actinic degradation and to microbiological attack. The manner in which the initial heating is carried out is of importance, oven heating causing appreciable amount of chemical degradation, which is believed to be a combined effect involving oxidation of the cellulose under the action of heat and the hydrolytic action of the liberated formic acid. Autoclave heating gives only slight damage.

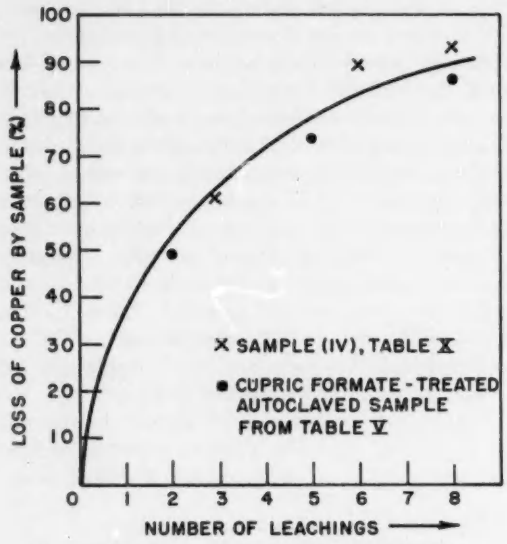

Fig. 1. Rate of loss of copper in ammonia leaching.

In view of the data given here, it is reasonable to conclude that the protection which the treatment gives to the fabric is the result of the comparatively substantial concentration of copper, in the form of cuprous oxide, on the fabric; that the fact that the copper is originally in the form of copper formate is of no particular significance; copper in other forms, not associated with a potentially nutritive anion, would in the above concentration give equally good results. Attention is drawn to the importance of this latter conclusion and it is emphasized that, in comparison with other organic compounds of copper, the apparent high efficacy of cupric formate as a treatment can be readily explained by the facts that, on heating, cupric formate decomposes to give copper in inorganic form (mostly Cu_2O), the organic anionic portion of the molecule decomposing to gaseous products and that other organic compounds of copper do not behave in this way. These reactions involving the reduction of the compound to the metallic oxide with complete loss of the organic portion of the molecule, when heated to moderate temperatures, are not, apparently, common to other organic compounds of copper.

The data obtained in this investigation do not support the view that the copper is in any special condition of association with cellulose. The treated cotton is freely soluble in standard cuprammonium

TABLE X. Retention of Copper on Ammonia Leaching with Intermediate Drying by Duck in which Cuprous Oxide had been Precipitated

	Unbleached duck containing Cu_2O Sample 2		Hydrocellulose containing Cu_2O Sample 4		Cupric formate treated autoclaved fabric from Table V	
Extent of ammonia rinsing	Copper, %	Copper remaining, %	Copper, %	Copper remaining, %	Copper, %	Copper remaining, %
None	0.26	—	1.22	—	0.73	—
At the end of 2 rinses; dried	—	—	—	—	0.37	50.7
At the end of 3 rinses; dried	0.11	42.3	0.48	39.4	—	—
At the end of 5 rinses; dried	—	—	—	—	0.19	26.0
At the end of 6 rinses; dried	0.051	19.6	0.13	10.6	—	—
At the end of 8 rinses; dried	0.043	16.5	0.083	6.8	0.10	13.7

solution and the copper in it can be substantially removed by repeated rinsing with dilute ammonium hydroxide, with intermediate drying. These findings do not suggest that there has been cross-linkage of the copper with the cullulose, nor does the observation that the copper in fabrics treated by the cupric formate process is rapidly and substantially completely removed during outdoor weathering over a period of four months—a performance no better than that shown by other compounds of copper, both inorganic and organic.

The data presented in this paper suggest that the copper in the treated fabric is mostly in the form of cuprous oxide (Cu_2O), which seems to be produced in considerable amounts when cupric formate is heated in air.

The incorporation into the surface of cotton fabric of cuprous oxide, as produced on reducing Fehling's Solution, affords protection against microbiological deterioration similar to that shown by cupric formate treated cotton.

Acknowledgment

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The Drying of a Mass of Hygroscopic Fibers by Forced Convection of Air: A Note on Some Physical Aspects

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Abstract

It is pointed out that, in drying of a uniform mass of fibers by forced convective air flow through the mass, a "drying front" proceeds through the mass in the same direction as, but much more slowly than, the air flow. Therefore, if uniform drying is to be obtained, the process must continue until the front has emerged from the downstream face of the mass of fibers; air of appropriate relative humidity must be used to leave the fibers at the desired regain; and reversal of air flow direction is undesirable on grounds of efficiency.

Calculations have been made of the capacity of air to remove water from a mass of wool fibers, the mass being left at given values of regain (4, 8, 12, and 16%). It is found that, except for the case of 4% regain, the capacity for water removal depends very little on the initial temperature of the air (in the range 30°–110° C.).

Introduction

Drying of a mass of fibers from the wet state is commonly effected in industry by forcing heated air through the mass until the required amount of water has been removed. This drying process usually involves the removal of all liquid water external to the fibers and some sorbed water from within the fibers. This note considers some physical aspects of the mechanism of water transfer from the mass to the air.

We shall assume that the fibers to be dried are arranged in a layer or bed approximately uniform in thickness and density of packing and that air of given temperature and moisture content is forced to flow uniformly through the bed. It is not always recognized, although it has been pointed out by Warburton [13], that under these conditions the drying process consists of the propagation of a "drying front" through the mass. This may be shown by a simple extension to the case of wet fibers of the theory developed by Cassie and others [1, 3, 4, 5, 8] for the case of air forced through a mass of fibers at a regain below saturation The simple theory postulates that initially air arriving at the upstream face of the layer becomes saturated instantaneously, falls in temperature to its wet-bulb value, and passes unchanged through the remainder of the mass. The mass becomes dried progressively from the upstream face, a sharp moving front dividing the downstream mass, with its original water content and at the wet-bulb temperature, from the upstream mass, which is in equilibrium in both temperature and regain with the incoming air. The front moves with a velocity u proportional to, but very much less than, the velocity v of the ingoing air. The difference between the moisture content of the ingoing air (expressed as mass of water per unit volume of air) and that of the same air saturated at its wet-bulb temperature gives the amount of water removed per unit volume of ingoing air. Denoting this latter quantity by w, we have

$$u = \frac{wv}{m}$$

where m = initial water content of unit volume of fibers.

The fact that drying proceeds by the propagation of a front through the mass leads to several important conclusions.

1. If the material is to be dried uniformly throughout, drying must proceed until the front reaches the downstream face of the layer. If the front remains within the mass, it is possible to achieve a particular

value of regain for the mass as a whole (by overdrying the fibers upstream from the front), but uniform drying is not possible. Once the front has emerged from the downstream face, no benefit is derived from any further flow of air.

2. The dried fibers upstream from the front are in equilibrium with the ingoing air. If the mass is to be dried to a particular value of regain the ingoing air must therefore be of the appropriate relative humidity. The use of air of lower humidity, e.g. in order to increase the rate of drying of the mass, will result in overdrying.

If the mass is to be uniformly dried, no control of the final regain is obtainable by adjustment of the rate of air flow or of the rate at which material is fed to the dryer.

3. It appears to be disadvantageous to reverse the direction of air flow during the drying process, although this is frequently done in industrial dryers. Reversal of flow direction leads to an increase in the regain of fibers which have already been dried.

There are some theoretical and practical considerations which call for certain modifications to the concept here adopted of a sharp front moving through the fiber mass, but these modifications do not affect the conclusions which have just been reached. One consideration is that at values of regain below saturation the assumption made in the simplified "front" theory [1, 3, 4, 5, 8] that the fibers are always in equilibrium with the air surrounding them is not strictly valid, and this has been shown [9] to cause the front to depart somewhat from the sharp form; a second consideration is that in practice air will flow more readily through some regions of the mass than through others, i.e., there will be "channelling," and the front will no longer be truly planar. These effects have a bearing on the efficiency of practical drying operations and are discussed in more detail in a paper [6] on that subject. However, the three conclusions previously reached remain valid provided the term "front" is taken to mean "trailing edge" in the case of a non-sharp front.

It is recognized that in some industrial drying operations uniform drying of the material may not be required, as long as a particular value of over-all moisture content is achieved; also, in some cases it is not practicable to prepare the material in a sufficiently uniform state for the front theory to be usefully applied. These cases are outside the scope of the present paper.

Clearly, in drying an assembly of fibers to a certain regain, the volume of air required is given by the expression (mass of water to be removed)/(mass of water removed per unit volume of air flowing). This volume of air may be drawn from an external source of the appropriate relative humidity, but it is common industrial practice to obtain the necessary volume by recirculation of the same air a number of times through the bed. After each passage the relative humidity must be reduced to the appropriate value, e.g. by heating. Recirculation reduces the volume of air to be taken in from the external source by a factor approximately equal to the number of passages of air through the layer before it is ejected at the exhaust. Recirculation provides one reason for heating the air in industrial textile dryers; indeed, it is probably the principal reason, as will be shown later.

It is of interest to investigate how the water-removing capacity of the ingoing air depends on its temperature, assuming that the fibers are to be left at a given value of regain. By way of example we shall consider the drying of wool. It is first necessary to find from published data [10, 11, 12] the equilibrium values of relative humidity at different temperatures for wool at the given regain. The calculations can then be carried through in several ways, of varying degrees of accuracy and convenience; these are discussed briefly in the Appendix. The results of such calculations are plotted as the curves of Figure 1, which show the water uptake capacity of input air as a function of air temperature, the wool being left at regains of 4, 8, 12, and 16%. An important fact indicated by the curves is that if the wool is to be

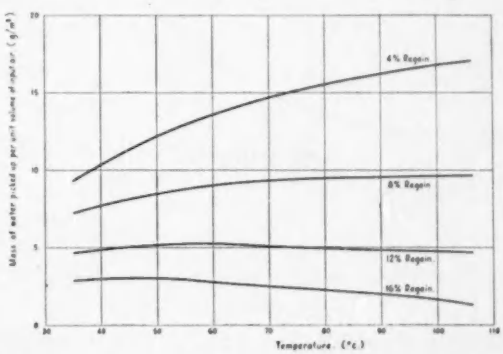

Fig. 1. Capacity of air to remove water from wet wool, leaving it at a particular value of regain, as a function of temperature.

left at regains in the range 12–16%, which is the range of usual interest, little or no increase in the drying capacity of the air is obtained by heating it. This is contrary to a commonly held view. Only when the wool is to be left at much lower regains does an increase in temperature raise the drying capacity of the air significantly. The physical reasons for this behavior depend on the interrelationship among regain, temperature, and moisture content of the air; they are not easy to see directly and are best discussed in connection with the diagram of temperature vs. moisture content of the air; this is done in the Appendix.

The small dependence on temperature for regains in the 12–16% range suggests that the use of unheated air as a practical drying medium for the textile industry is worth investigating, assuming that the lower temperature does not unduly prolong other processes affecting the drying such as diffusion of water from within the individual fibers. If the air is not to be heated, recirculation becomes impracticable; the air would be forced once through the layer and then discharged. The rate of air intake would therefore be much greater than in a dryer with recirculation. The characteristics, design, and possible advantages of such a dryer are examined in greater detail in another paper [6].

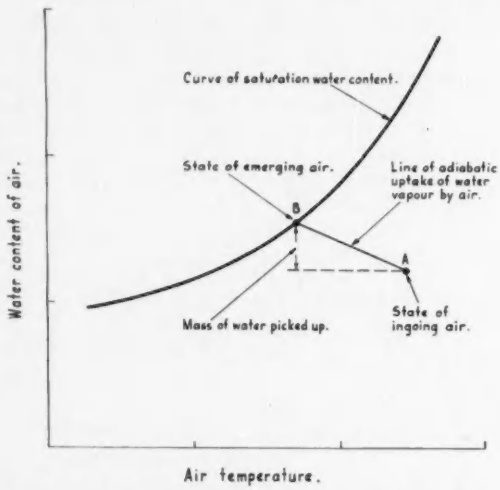

Fig. 2. Graphical solution of the case where air of initial water content and temperature represented by state A picks up evaporated water by an adiabatic process, reaching a final state B. The difference between ordinates of B and A represents the amount of water picked up.

Appendix

Determination of Amount of Water Picked Up; Its Dependence on Temperature

The problem is to find the amount of water picked up by air undergoing a process of adiabatic saturation [7], i.e., one in which the ingoing air becomes saturated by evaporation of water into it and falls in temperature, there being no exchange of heat between the system and its surroundings. The problem may be solved by finding the (linear) relationship between the temperature of the air and the amount of water picked up by it under adiabatic conditions and then determining by a graphical method where this relation is satisfied simultaneously with the condition that the air is saturated. The method is illustrated graphically in Figure 2; it is accurate, but tedious in that a separate graphical construction is needed for each determination.

An alternative method is to regard the system as a wet-bulb hygrometer and to assume that the outgoing air is at the appropriate wet-bulb temperature; then from tables the saturation water content of air at this temperature is found and from it is deducted the water content of the ingoing air. The method is simple but under some conditions is of poor accuracy, in that it involves taking the (small) difference between two large quantities.

A compromise method regarding the system as a wet-bulb hygrometer but having adequate accuracy is to find as in the first method the linear relationship between air temperature and mass of water evaporated and to evaluate it for a temperature drop equal to the wet-bulb depression of the ingoing air, as found from tables. The method has been checked against the first-mentioned one and found to agree satisfactorily; an example will illustrate its use.

Consider a mass of ingoing moist air such as to contain unit mass of dry air. Let the moisture content be W g./g. of dry air. Then the ingoing mass is $(1 + W)$ g. Let this air be cooled and saturated, the temperature drop being ΔT and the increase in mass, i.e., the amount of water picked up, be Δm. Then it can be shown [2], if the process is adiabatic, that

$$(1 + W)C_p\Delta T + L\Delta m = 0 \qquad (1)$$

where C_p = specific heat of ingoing moist air (the specific heat at constant pressure is the appropriate quantity) and L = latent heat of evaporation of

water (at the wet-bulb temperature). From Equation 1

$$\Delta m = -\frac{(1 + W)C_p}{L}\Delta T \qquad (2)$$

The quantity $(1 + W)C_p$ is the heat capacity of a mass of moist air containing unit mass of dry air, and is the sum of the heat capacities of its constituents; i.e.,

$$(1 + W)C_p = C_{p_{air}} + WC_{p_{vap}} \qquad (3)$$

where $C_{p_{air}}$ and $C_{p_{vap}}$ are the specific heats at constant pressure of dry air and water vapor respectively. Substituting Equation 3 in 2, we get

$$\Delta m = -\frac{C_{p_{air}} + WC_{p_{vap}}}{L}\Delta T \qquad (4)$$

To take a numerical example, we shall find the water-removing capacity of air entering the wool at 45° C. and at a relative humidity such as to leave the wool at 12% regain. From published data [10] the required relative humidity is found to be 47.3%. The corresponding value of W is computed from the known partial pressures and is found to be 2.91×10^{-2} g./g.; from psychometric tables the wet-bulb temperature is found to be 34.3° C. (whence $\Delta T = 10.7°$ C.). L at 34.3° C. = 577 cal./g., $C_{p_{air}} = 0.242$, and $C_{p_{vap}} = 0.446$. Substituting these values in Equation 4, we find $\Delta m = 4.75 \times 10^{-3}$ g./g. of dry air at the input.

To express this in terms of volume of ingoing air, the specific volume of the input is computed (again from the known partial pressures) as 9.45×10^{-4} m.³/g. of dry air. Hence the amount of water removed is 5.03 g./m.³ of input air.

The reason that the curves of Figure 1 for 16, 12, and 8% regain are nearly horizontal (i.e., temperature independent) may be seen by applying the construction outlined in Figure 2 to the family of curves presented in Figure 3, which shows the relationship between temperature and water content of the air for wool at several values of regain (wool in the desorption state); i.e., each curve of Figure 3 is the locus of all air conditions which are in equilibrium with wool of a particular regain. As an example, the points P, Q, R, and S represent various states of air which are in equilibrium with wool of 12% regain, and the lines PW, QX, RY, and SZ are lines representing the process of adiabatic uptake of water, interesecting the saturation vapor density curve at W, X, Y, and Z. The amount of water picked up by air initially at point P is given by the difference between the ordinates of points P and W; similarly for air at the other initial states. Since the curves PQRS and WXYZ are nearly parallel, these differences are nearly independent of temperature. The curve for 12% regain in Figure 1 indicates this fact.

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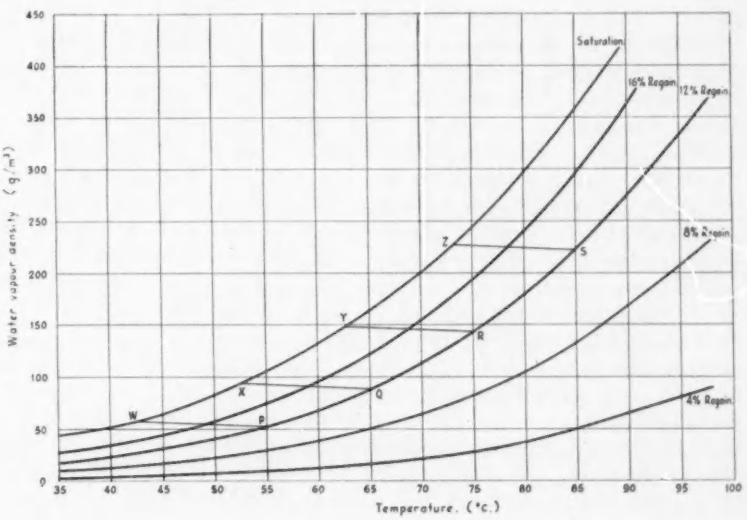

Fig. 3. Curves relating temperature and water content of air which is in equilibrium (in desorption) with wool of particular values of regain.

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The Plasticity of Wool

Part IV: The Effect of Variations in Nutrition

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Abstract

The plasticity of wool increases, and the difference of plasticity between fibers from primary and secondary follicles is accentuated, as the level of nutrition of the sheep decreases.

IT HAS been shown in a previous paper [1] that the variations in plasticity among the fibers of a single staple of wool are associated with the different types of follicle from which the fibers are derived. Since there is an inverse relationship between the plasticity of the fibers and the order of development of the follicles, it seemed probable that the differences in plasticity are brought about by competition for the available nutrition. Samples of wool supplied by Mr. H. B. Carter of the Animal Breeding Research Organization, Edinburgh, have made it possible to test the truth of this deduction, as well as to study the general effect of differences in the level of nutrition of the sheep on the nature of the wool produced.

The wools examined were taken from a pair of South Australian merino sheep which exhibited, as lambs, such very similar fleece characteristics as to suggest that they were one-egg twins. The animals were reared under rigidly controlled conditions, one twin being maintained on a continuous high plane of nutrition, the other on a low plane, from lambs to the age of 3–4 years. In addition, the samples were grown under rugs to minimize the effect of weathering. The fibers used represented 176 days' growth in the second year, and varied in length from 5 to 17 cm., but only a few fibers from each length group were available for examination. These were purified by extraction with ether in a Soxhlet apparatus, followed by repeated washing in cold alcohol and water. In determining plasticity, the length of fiber used was proportional to the total length in order to minimize the effect of any variations in conditions during the period of growth. The values of the plasticity constant k, derived from observations of the rate of creep of the fibers under a load of 6 kg./mm.^{2} in distilled water at 22.2° C., are given in Table I, the empirically chosen limiting extension being 54% in all cases. The difference between the two groups is highly

TABLE I. Plasticity of Fibers Grown Under High and Low Levels of Nutrition

Level of nutrition	Number of fibers	Mean diameter, μ	Plasticity, k, arbitrary units
High	22	40.3	16.5
Low	18	33.0	22.9

TABLE II. Differences in Plasticity of Primary and Secondary Fibers Grown Under High and Low Levels of Nutrition

Level of nutrition	Type of fiber	Number of fibers	Mean diameter, μ	Plasticity, k, arbitrary units
High	Primary	12	51.0	14.3
	Secondary	10	27.4	19.2
Low	Primary	10	43.0	16.2
	Secondary	8	20.7	31.3

significant (t = 2.61, 38 degrees of freedom, t required at the 1% level of significance = 2.70, at the 5% level = 2.02), showing that the fine structure of fibers grown under a restricted level of nutrition has a lower resistance to extension, due, presumably, to a lower cystine content [2].

As the longest and thickest of the fibers examined are likely to be derived from primary follicles, the results were next divided into two groups on the basis of fiber volume. Fibers exceeding the mean fiber volume of each group were classified as primaries and the rest as secondaries. The data are given in Table II. The most striking effect of restricted nutrition is the large increase in the plasticity of the secondary fibers. Whereas the difference between primaries and secondaries on the low plane is very highly significant (t = 4.54, 16 degrees of freedom, t required at the 1% level = 2.92), the corresponding difference on the high plane is smaller (t = 2.25, 20 degrees of freedom, t required at the 1% level = 2.85, at the 5% level = 2.09).

The above results are of special interest in relation to the farmer's belief that wool grown on poor country is of superior quality. When supposedly fine-wooled sheep are moved to better pastures, the quality of the wool may deteriorate, and while this is generally explained in terms of dimensional changes, it now seems clear that "hunger-fine" wools may also have superior physical properties for particular purposes.

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